X-RAY CRYSTALLOGRAPHIC STUDIES OF SOME DERIVATIVES OF DICOBALTOCTACARBONYL AND TETRACOBALTDODECACARBONYL WITH PI BONDING LIGANDS

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ABSTRACT

X-RAY CRYSTALLOGRAPHIC STUDIES OF SOME DERIVATIVES OF DICOBALTOCTACARBONYL AND TETRACOBALTDODECACARBONYL WITH PI BONDING LIGANDS

ALAN RICHARD FRASER

SIR GEORGE WILLIAMS UNIVERSITY, 1973.

This Thesis describes the results of X-ray crystallographic structure determinations on five organometallic complexes which all involve cobalt metal-metal bonds and π bonded organic ligands such as acetylenes and arenes.

The first structure reported is that of tris(hexacarbonyldicobalt-π-ethynyl)arsine which is a product of the reaction of triethynylarsine and dicobaltoctacarbonyl. The molecule possesses a *pseudo* three-fold axis with a dicobalthexacarbonyl fragment π bonded to each acetylenic linkage. The acetylene-cobalt geometry is discussed.

The structures of two substitution products of dicobalthexacarbonyldiphenylacetylene with $Ph_2MCH_2MPh_2$ where Ph = phenyl and M = P or As were also investigated. The complexes $Co_2(CO)_4(PhCCPh)(Ph_2PCH_2PPh_2)$ and $Co_2(CO)_2\cdot(PhCCPh)(Ph_2AsCH_2AsPh_2)_2\cdot 1,2\text{-}C_2H_4Cl_2$ include chelating

diphosphine and diarsine ligands, respectively, which bridge the cobalt-cobalt bond. The diphenylacetylene is also found to bridge the cobalt-cobalt bond.

Finally, two products of the reaction of arenes with tetracobaltdodecacarbonyl were investigated by X-ray crystallography. The mixed crystal of *ortho*- and *meta*-xyleneenneacarbonyltetracobalt as well as the complex benzene-enneacarbonyltetracobalt are reported. Both compounds display an arene π bonded to the apical cobalt atom of a tetrahedral $Co_4(CO)_9$ cluster. The bonding features of the arene ring are discussed.

RESUME

ETUDES DES STRUCTURES CRISTALLINES ET MOLECULAIRES DE QUELQUES DERIVES DU DICOBALTOCTACARBONYLE ET DU TETRACOBALTDODECACARBONYLE AVEC DES LIAISONS COORDONNEES A CARACTERE PI

ALAN RICHARD FRASER

UNIVERSITE SIR GEORGE WILLIAMS

Cette thèse est le compte rendu des études cristallographiques de cinq composés organométalliques à liaison cobalt-cobalt coordonnée par des liens pi aux acétylènes ou aux hydrocarbures benzéniques.

La première structure étudiée est celle du tri(hexacarbonyledicobalt-π-éthynyle)arsine, produit par réaction du tri-éthynylarsine sur le dicobaltoctacarbonyle. La molécule possède un axe *pseudo*-trigonale. Chacune des liaisons acétyléniques est pontée par un fragment dicobalt-hexacarbonyle.

Les structures de deux produits de substitution du dicobalthexacarbonylediphénylacétylène avec $Ph_2MCH_2MPh_2$ (Ph – phényle et M – P ou As) ont été étudiées. Dans les structures $Co_2(CO)_4(PhCCPh)(Ph_2PCH_2PPh_2)$ et $Co_2(CO)_2(PhCCPh)\cdot(Ph_2AsCH_2AsPh_2)_2 \cdot 1,2\text{-}C_2H_4Cl_2$, les deux atomes de cobalt sont pontés par les deux atomes de phosphore chez les

diphosphines et par les deux atomes d'arsenic chez les diarsines.

Deux produits de la réaction des hydrocarbures benzéniques avec le tétracobaltdodécacarbonyle ont été étudiés par les méthodes cristallographiques. Le système *o*-xylène- et *m*-xylène-nonacarbonyletétracobalt qui présentent un phénomène de désordre local et le complexe benzène-nonacarbonyletétracobalt sont exposés. Chez ces derniers, les hydrocarbures aromatiques forment une liaison pi avec la tête du tétrahèdre $Co_4(CO)_9$.

This Thesis is

Dedicated

to my father,

the late

William Fraser.

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Thanks are also due to John Lawson and David Hall for helpful discussions and especially, for their encouragement when research went badly and the end seemed nowhere in sight.

Finally, I would like to thank my mother, Mrs. Irene Fraser, for her patience and understanding.

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CHAPTER I. GENERAL INTRODUCTION.

The prime objective of this Thesis is to present the results of single crystal X-ray crystallographic structure determinations of five novel organometallic complexes synthesized in this laboratory. These five complexes have the common feature that they are all π bonded derivatives of either dicobaltoctacarbonyl ($Co_2(CO)_8$) or tetracobaltdodecacarbonyl ($Co_4(CO)_{12}$). Their differences however have forced their segregation into three separate chapters representing separate compound classes.

It was deemed necessary to introduce properly each class by reviewing the structural research which precedes this work. In this way, the reader will not find it necessary to go to external sources to familiarize himself with the material. Furthermore, the original work reported in this Thesis will thus be placed in context while maintaining a sharp division with the work done by others. Each of the three chapters (III to V) contains three sections; 1) an introduction, 2) an experimental section and 3) a results and discussion section. Chapter II presents general experimental techniques used for all chemical and crystallographic studies. Finally, a six part Appendix gathers together chemical and crystallographic data which are either of secondary importance to the body of the Thesis or which constitute the pre-treated data.

X-ray crystallographic techniques have now become commonplace within the confines of molecular structural research. With modern automated diffractometers, the undertaking of a structural problem by X-ray crystallography no longer represents a major technical challenge, although it is not altogether routine. A recently published note [1] by Cotton and Troup describes, as summarized by the title, "... X-ray Crystallography as a Practical Means of Cheap, Rapid and Definitive Analysis". In view of the fact that four structures were solved, each within 7.5 working man hours through an average elapsed time of 84 hours at an average computing cost of 139 dollars, it is difficult to refute this claim. The reader must bear in mind, however, that the term 'solved' means to isotropic convergence only. The time and money-consuming intricacies of anisotropic refinement as well as various corrections and improvements are not included. The accuracy of Cotton's structure determinations is limited. To carry a single crystal X-ray structure determination to the point where sound theoretical arguments can be made based on bond and angle differences requires considerably more time and money.

Many review articles have been published on the transition metal carbonyls [2 - 6], with a large concentration on the structural aspects. Cotton and Wilkinson[7] have presented a rather clear picture of the bonding of carbon monoxide to transition metals. Chemical as well as physical contradictions have led to an explanation of the bonding of CO to transition metals in terms of a synergic bonding mechanism. According to this multiple bonding scheme,[8] there is dative bonding between a filled carbon σ orbital of CO and the metal accompanied by the simultaneous dative overlap of a filled $d\pi$ metal orbital with an empty $p_{\pi}*$ orbital of CO. Since this antibonding orbital is becoming populated, the C≡O bond is consequently weakened. This effect is most clearly observed in the approximate 150 cm^{-1} drop in the C≡O stretching frequency when comparing free :C≡O: (2143 cm^{-1}) with a terminal transition metal carbonyl ligand.

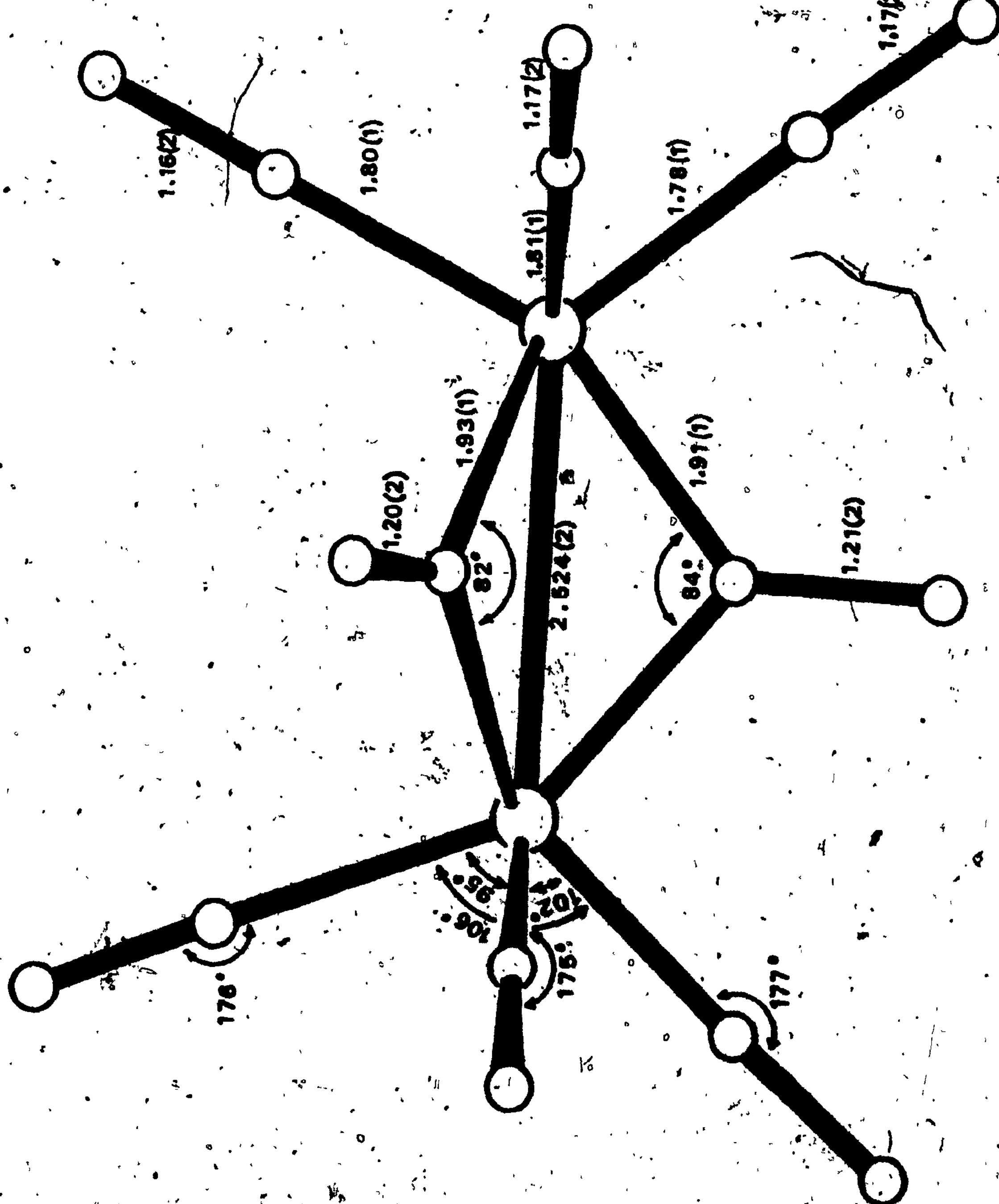
The carbonyl ligand has been observed to be both terminal and bridging. There is also a possibility that the bridge may be two point or three point. Usually bridging carbonyl ligands help keep the metals in sufficiently close proximity to allow bonding between them.

In solution, it is claimed that some structures interconvert between bridging and non-bridging forms. This stereochemical non-rigidity has been studied by Bullitt, Cotton and Marks[9,10] for $((h^5\text{-}C_5H_5)Fe(CO)_2)_2$ by nuclear magnetic resonance (nmr) spectroscopy. Similar interconversion has been proposed for $Co_2(CO)_8$ and $Co_4(CO)_{12}$, the two most frequently encountered cobalt carbonyl complexes. The remainder of this Introduction is dedicated to an examination of these two compounds, precursors of the products reported in this Thesis.

When Sumner *et al.*[11] finally published the results of a single crystal X-ray crystallographic structure determination of $Co_2(CO)_8$, five different geometries had been proposed for its structure using various physical methods. Two independent $Co_2(CO)_8$ molecules were discovered in the asymmetric unit (both lying on a mirror plane). The bond lengths and angles reported here (Figure I-1) are a weighted mean. The co-ordination about the cobalt atom is distorted octahedral (d^2sp^3 hybridization). The Co-Co bond length is reportedly 2.524(2)Å. Infrared spectral analysis of $Co_2(CO)_8$ in solution[12] suggested that only the bridged form existed in solution but evidence for the unbridged form was given at a later date.[13] It seems reasonable now to assume that the two structures are interconverting in solution at room temperature.

Such an interconversion has been shown by Cotton and co-workers for tetracobaltdodecacarbonyl ($Co_4(CO)_{12}$). The idea was originally proposed in 1966[14] on a purely hypothetical basis. In 1972, Cotton *et al.*[15] proved rapid scrambling of the CO groups in $Rh_4(CO)_{12}$ by ^{13}C nmr and

Figure I-1. A schematic representation of the molecular geometry of dicobaltoctacarbonyl with pertinent bond lengths and angles as taken from Ref. 11 .


1.16(2)
1.80(1)
1.17(2)
1.81(1)
1.78(1)
1.17(2)
1.93(1)
1.91(1)
1.20(2)
82°
2.624(2)
84°
1.21(2)
96°
106°
120°
175°
176°
177°

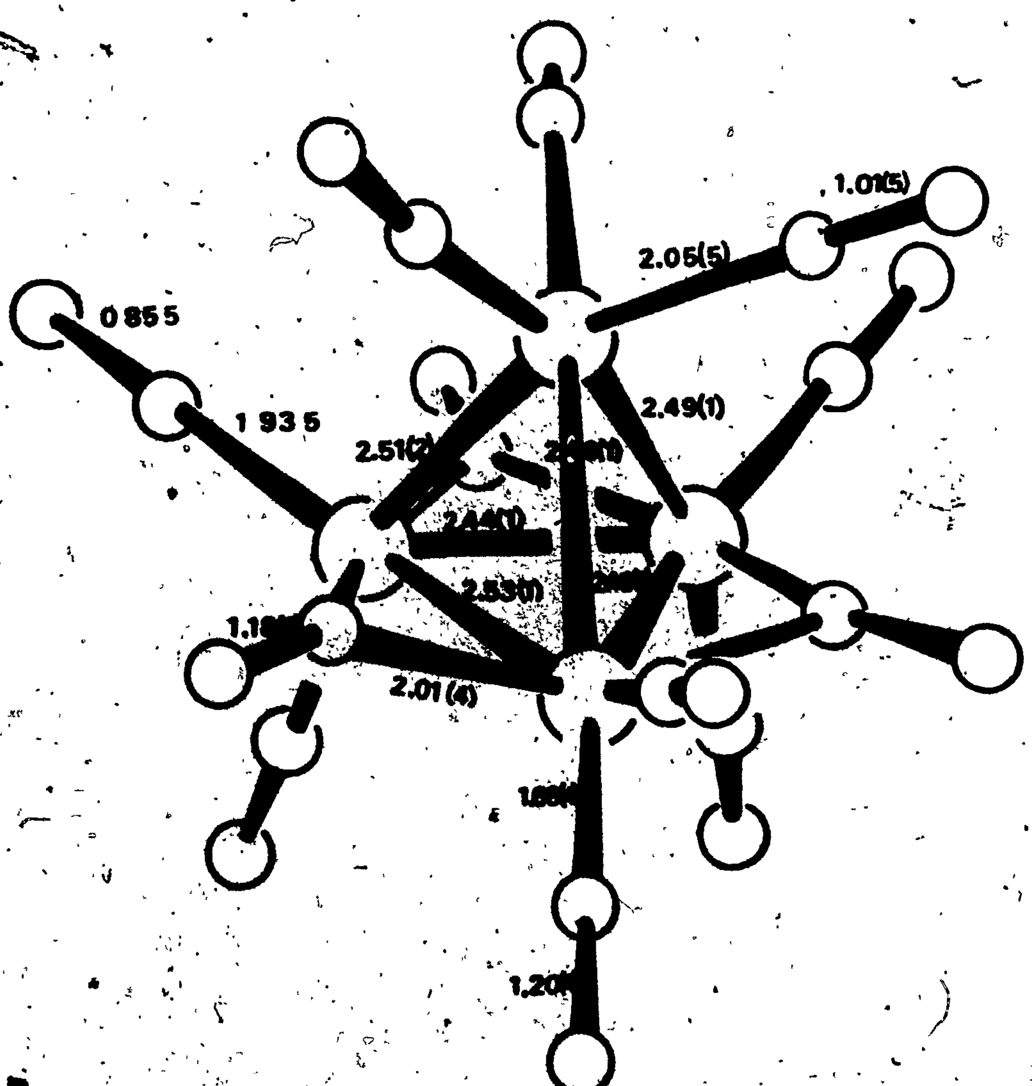
extrapolated these findings to the complex $Co_4(CO)_{12}$.

Corradini[16] first published a two-dimensional X-ray study of $Co_4(CO)_{12}$ which was far from detailed but which did indicate positively that a tetrahedron of cobalt atoms was present. Various infrared studies[17-21] supported this model but arguments remained over the nature of the bonding of the 12 carbonyl groups. This controversy was settled by a single crystal X-ray structure determination of the disordered $Co_4(CO)_{12}$.[22,23]

The crystals of $Co_4(CO)_{12}$ studied by Wei consist of two-fold disordered tetrahedral clusters of cobalt atoms which give rise to a *pseudo* two-fold axis. Bond lengths and angles for an asymmetric unit were calculated and, applied to a single $Co_4(CO)_{12}$ molecule, can be seen in Figure I-2. The average carbonyl-bridged basal Co-Co distance is 2.485(14)Å whereas the basal-to-apical cobalt distances average 2.494(16)Å. The compound has been classified as a closed metal carbonyl cluster (CMCC) 6/7/7/7 by Chini.[24]

$Co_4(CO)_{12}$ was first synthesized[25] by the thermal decomposition of $Co_2(CO)_8$ (Equation I-1). Recently Ungváry and Markó[26] have published an article on the kinetics and mechanism of this thermal decomposition. The rate-determining step is the dimerization of two $Co_2(CO)_6$

Figure I-2. A schematic representation of the molecular geometry of tetracobaltdodecacarbonyl with pertinent bond lengths and angles as taken from Ref. 23 .


1.01(5)
2.05(5)
0 85 5
1 93 5
2.49(1)
2.51(2)
2.44(1)
2.53(1)
2.01(4)
1.20(

units to form $Co_4(CO)_{12}$. These units are formed from $Co_2(CO)_8$ by the successive loss of one, then another mole of CO gas.

$$2Co_2(CO)_8 \longrightarrow Co_4(CO)_{12} + 4CO\uparrow \qquad \text{I-1}$$

Finally, it must be added that the form, the abbreviations and the presentation of references used in this Thesis are all according to the American Chemical Society.[27]

CHAPTER II. GENERAL EXPERIMENTAL TECHNIQUES.

SECTION A. CHEMICAL

Chemical reactions reported in this Thesis were carried out in an Erlenmeyer flask with sidearm under an atmosphere of pre-dried nitrogen gas. A water-cooled reflux condenser was in turn connected by an airtight link to a mercury bubbler. The reaction mixture was stirred using a magnetic stirrer which was combined with a hotplate.

The chemicals used in these reactions were obtained from the manufacturers listed in Table II-A-1 and, for the most part, were used without further purification. The solvents were dried over calcium hydride or lithium aluminum hydride by refluxing for several days. They were distilled in an atmosphere of nitrogen gas. The solvents used for infrared spectroscopy and nmr spectroscopy were not purified.

The chromatographic columns that were used varied in diameter and length. Silica gel powder (60-200 mesh from the J.T. Baker Co.) was invariably used. It was

TABLE II-A-1

SOURCE OF CHEMICALS AND SOLVENTS

Chemicals:

Acetylene ('Presto-lite' dissolved)	Linde Chemical
Aniline (mp -7^{o} to -6^{o}C)	Canlab[a]
Benzene (Reagent)	Fisher[b]
Bromoethane (Practical)	Fisher
Benzonitrile (Reagent)	Fisher
Dicobaltoctacarbonyl (Assay 98%)	Alfa Inorganics
o-xylene (Reagent)	Fisher
m-xylene (Reagent)	Fisher
p-xylene (Reagent)	Fisher
Hexachlorobenzene (Practical)	Fisher
Hexaethylbenzene (Highest Purity)	Aldrich Chem. Co. Ltd.
Hexafluorobenzene (Highest Purity)	Aldrich Chem. Co. Ltd.
Hexamethylbenzene (Reagent)	Eastman Kodak Co. Ltd.
Magnesium metal filings (Grignard)	Fisher
Toluene (Practical)	Eastman Kodak Co. Ltd.
Tetracobaltdodecacarbonyl	From $Co_2(CO)_8$
Trichloroarsine(III) (Reagent)	Baker and Adamson Ltd.
ααα-trifluorotoluene (Practical; bp 100-102^{o}C)	Canlab
1,3,5-trihydroxybenzene (Practical; bp 217-219^{o}C)	Fisher
1,3,5-trimethylbenzene (Practical; bp 160-163^{o}C)	Eastman Kodak Co. Ltd.

TABLE II-A-1 (CONT'D)

1,3,5-trinitrobenzene (Practical; 10% water)	Eastman Kodak Co. Ltd.
Solvents:	
Chloroform (N.F.)	Fisher
Cyclohexane (Certified)	Fisher
Dichloromethane (Certified)	Fisher
Diethylether (Practical)	Fisher
Hexane (Technical)	Anachemia Chemicals
Ligroin (bp 66°-75°C)	Fisher
Tetrahydrofuran (Certified)	Fisher
Carbon disulphide (Certified Spectroanalyzed)[b]	Fisher
Tetrachloroethylene (Reagent)	J.T. Baker Chem. Co.
Miscellaneous:	
Calcium hydride (Purified)	Fisher
Lithium aluminum hydride	Alfa Inorganics
Glyptal cement	General Electric

a Canadian Laboratory Supplies Limited
b Fisher Scientific Company Limited

sometimes deactivated with water and the columns were always packed wet and topped with fine sea sand.

Chemical analyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee, United States of America.

Melting points were measured on a Gallenkamp melting point apparatus. A sample of the compound was crushed to a powder and packed in a capillary tube which was flushed with nitrogen gas and sealed with putty. The melting points were not corrected.

Most infrared spectra were recorded on a Perkin-Elmer grating infrared double beam spectrophotometer model number 457. Peak frequencies are reported to $\pm 3cm^{-1}$. Some spectra were recorded on a Perkin-Elmer grating infrared double beam spectrophotometer model number 225. Peak frequencies can be reported to $\pm 1cm^{-1}$ for this instrument. Spectra from both instruments were calibrated using a polystyrene film at 2850.7, 1601.4, 906.7 and $698.9cm^{-1}$. Abbreviations used in tables quoting infrared frequencies are: vs - very strong, s - strong, m - medium, w - weak, sh - shoulder, bd - broad.

Unless otherwise specified, 1.0 mm matched sodium chloride cells (Beckman) were used for the solution spectra. Potassium bromide windows were used for the NUJOL mull spectra with a 0.01 mm spacer in a demountable infrared cell (Research and Industrial Instruments Co.).

The proton magnetic resonance spectra were recorded on a Varian A60-A spectrometer. The chemical shifts quoted are those relative to tetramethylsilane used as an internal standard. Mass spectra were recorded using a Hitachi Perkin-Elmer double-focusing mass spectrometer model number RMU-6E.

All density measurements were done by the flotation method. The crystal was placed in a solution whose density was adjusted until the crystal neither moved upward or downward in the body of the solution. The density of the solution (assumed equal to that of the crystal at this point) was measured using a 10.0 ml pycnometer. The volume of the pycnometer had been previously determined so that the density of the solution, and thus the crystal, could be calculated.

SECTION B. CRYSTALLOGRAPHIC

1. Space Group Determination

A crystal, large enough to see but too small to tell its shape with the naked eye, was selected which appeared to be single and whole under microscopic examination. This crystal was afixed to a borosilicate glass fibre using glyptal cement. The fibre was in turn fixed securely to flexible copper wire attached to a goniometer head. The head was mounted on the goniometer to determine the elevation that would allow centering of the crystal in the diffractometer beam. This setting was subsequently not varied.

Weissenberg and oscillation photographs were obtained on a Charles Supper Co. Weissenberg camera. Both the Weissenberg and the precession camera (also made by the Charles Supper Co.) were operated using a fine focus molybdenum X-ray tube. This was powered at 40kV and 20 mA by a Picker Nuclear X-ray generator and control model number 809B. Ilford 'Industrial-G' film and Kodak 'No-Screen' film were used during the course of these investigations.

The Weissenberg geometry was such that 1 mm on the zero level photograph corresponds to 2°. The relationship between the film-measured spacing y_n and the reciprocal cell constants for the precession camera is illustrated in Figure II-B-1 and by Equation II-B-1. The film-to-crystal distance for the zero level precession zones was 60.0 mm. The wavelength of the molybdenum radiation filtered with zirconium foil was taken as 0.71069Å. The circle in Figure II-B-1 is a two-dimensional representation of the sphere of reflection through which a reciprocal lattice point must pass in order to ensure diffraction.

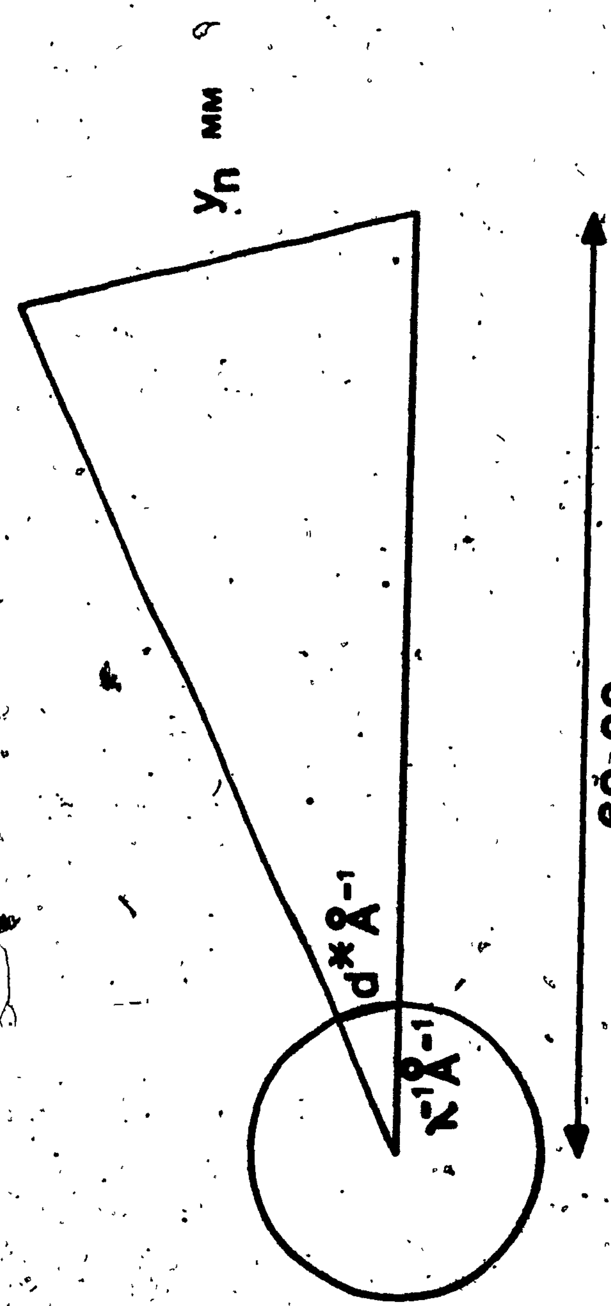
$$d^* = \frac{y_n}{60.0\ \lambda} \qquad \text{II-B-1}$$

2. Data Collection

A Picker Nuclear automated four-circle diffractometer operated by a P.D.P. 8/S dedicated mini-computer was used for data collection. A Picker Nuclear constant potential diffraction generator model number 6238E (stable to within 0.1% kV and 0.02% mA) provided the power (40 kV 18 mA) for a molybdenum X-ray tube. The takeoff angle was 3.0° for the direct beam and this was monochromated using the (002) face of a graphite monochromator 'crystal'.

The 0.71069Å K_α radiation of molybdenum was passed through a 1 mm diameter pinhole collimator directed

Figure II-B-1. The relationship of reciprocal space and precession geometry.



y_n MM
d^* Å^{-1}
λ^{-1} Å^{-1}
60.00 MM

at the sample crystal. The sample was situated 14.0 cm from the point at which the X-rays were monochromated. Diffraction at the crystal took place in a plane perpendicular to that of monochromation. A receiving aperture whose size was determined by horizontal and vertical slits was located 23.0 cm from the crystal and 20 mm from a scintillation counter.

A series of three nickel foil attenuators on a rotating disc were located at the aperture. The detector was operated at about 1000 volts (5.60 helipot setting) and a pulse height analyzer was set to receive 100% of the X-ray intensity. A scan, using a 0.2keV window (upper level setting of 2.0 and 10% mode), of peak intensity versus baseline discriminator level was recorded from 10.0 keV to 0.6 keV. The differential pulse height distribution curve so obtained was used to establish the upper and lower level of discriminator voltage for 100% peak acceptance.

Weissenberg angles on the goniometer head were set and it was mounted on the diffractometer. A strong reflection was chosen from the zero level Weissenberg and its measured 2θ angle was set on the diffractometer. Values of ω, χ and ϕ were set to zero and ϕ was scanned until the reflection chosen was located. Scanning 2θ at this predetermined ϕ value confirmed the axial diffraction intensity pattern.

Another reflection was located on the zero level and these two reflections were centered using a P.D.P. 8/S computer alignment program supplied by the Picker Nuclear Co. For this process, the slits in the receiving collimator were partly shut to ensure higher accuracy. The crystal was systematically mis-set, first in 2θ and ω, and subsequently in χ and ω for the centered 2θ angle. Counting at each angular setting was for 10 second periods. Location of half intensity on both sides of the peak permitted the computation of the peak center. The two centered reflections were used in conjunction with the film-measured unit cell parameters to locate the third axis.

Twelve reflections were chosen in such a way that their intensities and their 2θ angles were sufficiently high and that their positions covered the surface of reciprocal lattice reflections evenly and completely. These were centered using the method described above. Accurate values of 2θ, ω, χ and ϕ were obtained at both $+2\theta$ and -2θ (for the hkl and $-h$-k-l reflections,respectively) and the results were averaged.

The input parameters to the least squares refinement were the six approximate cell constants and ω, χ and ϕ for a primary and a secondary reflection (chosen such that their χ angles were close to 0° and their ϕ angles were separated by about 90°). Of these input parameters, the following only were refined: the variable cell parameters, ω and χ of the primary reflection and χ of the secondary reflection. The estimated standard deviations of the cell parameters quoted were computed as a result of the least squares refinement. The refined ω and χ values of the primary and secondary reflections were used to compute an orientation matrix for the crystal which was then used for data collection.

The reflections comprising the three reciprocal unit cell axes were measured before data collection was started. Their intensities were compared to those measured after data collection to ensure the stability of the crystal and of the instrument. The θ-2θ scanning method was used to record the integrated intensity of the reflections. The crystal was moved slowly (1^{o} per minute) so that the reflection being measured passed through the sphere of reflection in its equatorial plane. The length of the scan, specified for low angle reflections, was determined. This varied according to the mosaicity of the crystal examined and the value of 2θ. At high values of $(\sin\theta)/\lambda$, the difference between α_1 and α_2 diffraction is more pronounced than at low angles. To allow for this α_1-α_2 dispersion, a factor of 0.692 for Mo K_α radiation was used by the Picker Nuclear data collection program to compute the angular scan length for every reflection.

Beyond 10^4 cps, attenuators made of nickel foil and calibrated to factors of 2.781, 7.959 and 38.190 were automatically inserted in the aperture for the most intense reflections. To ensure that the crystal was not deteriorating or changing its position in relation to the orientation matrix during the collection of data, check reflections were measured at regular intervals. In most cases, three reflections (usually axial) were monitored. Most often these reflections varied in harmony and one was chosen to scale the data.

A maximum and a minimum 2θ value was specified. The limits of h, k and l determined the portion of the sphere to be collected. A routine was introduced into the program used for automated data collection to prevent the futile measurement of systematically absent reflections. The data were recorded on punch paper tape. These were transferred to magnetic tape with the use of the 2114A Hewlett Packard computer.

3. Data Reduction

All computing was accomplished on the Control Data Corporation (C.D.C.) 3300 computer for the tris(hexacarbonyldicobalt-π-ethynyl)arsine structure and on the C.D.C. 6400 computer for the other structures reported in this

Thesis. It was found that convergence of least squares refinements occurred somewhat more rapidly with the latter computer probably due to the 64 bit word as opposed to the 48 bit word of the C.D.C. 3300.

Data reduction was accomplished using a locally-written program called *PREP*. All the counts were brought to a common basis by applying the attenuator factors (where used) to the peak counts and the backgrounds. The intensity of the strongest selected check reflection was used to scale the data to a common standard for all reflections. The mean atomic scattering factors, at intervals of $(\sin\theta)/\lambda$ of 0.05Å^{-1}, for all atoms were obtained from the computations of Ibers and others.[28a,b] The program interpolates a form factor f_j for an atom j depending on the particular $(\sin\theta)/\lambda$ value of the reflection concerned.

The value of the reflection intensity I was computed according to Equation II-B-2. N is the peak count in the scan time t_s seconds, and B_1 and B_2 are the background counts on either side of the peak each measured for t_b seconds. If I was computed to be less than 0.0, the reflection was considered absent. The standard deviation of the intensity I was computed according to Equation II-B-3. If the intensity I was less than $3\sigma(I)$, the reflection was considered to be invalid based on counting error. Along with the absent reflections, these reflections were rejected and used neither for structure solution nor refinement (except when normalized structure factors were calculated).

$$I = N - \left[B_1 + B_2\right] t_s / 2t_b \qquad \text{II-B-2}$$

$$\sigma(I) = \left[N + \frac{(B_1 + B_2)}{2}\left(\frac{t_s}{t_b}\right)^2 + (0.02N)^2\right]^{\frac{1}{2}} \qquad \text{II-B-3}$$

Computation of relative structure factors F_{rel} (from the intensities I) depends upon X-ray polarization and Lorentz corrections. While it is true that F_{rel} is proportional to the square root of I, corrections must be made for the polarization of X-rays by the monochromator crystal. Corrections must also be made for the diffraction-angle-dependent velocity of a reciprocal lattice point passing through the sphere of reflection. This is termed the Lorentz correction. A combined term Lp which is specific to the diffractometer geometry used, is defined in Equation II-B-4 (where θ_s and θ_m are the diffraction angles at the sample crystal and the monochromator crystal respectively). The relative structure factor was thus computed by the program using Equation II-B-5. The rate of change of F_{rel} was obtained from the derivative of Equation II-B-5 and is called *sigma*. *Sigmas* were calculated for all the reflections accepted by the program.

$$Lp = \frac{(\cos^2 2\theta_m + \cos^2 2\theta_s)}{\text{sine } 2\theta_s\,(\cos^2 2\theta_m + 1)} \qquad \text{II-B-4}$$

$$|F_{rel}|_{hkl} = \left[\frac{I_{hkl}}{Lp}\right]^{\frac{1}{2}} \qquad \text{II-B-5}$$

The program *PREP* also treats the reflection statistics to predict the absolute scale factor relating F_{abs} to F_{rel} and an approximate overall thermal parameter. Such information was obtained from the reciprocal of the slope and from the intercept, respectively, of the linear Equation II-B-6 which is derived from Equation II-B-7. $\overline{I_{rel}}$ is the average F^2_{rel} value and f_{oj} is the mean atomic scattering factor for the j^{th} atom. The thermal parameter B was thus derived from the slope of a plot of $\ln(\overline{F_{rel}}/\Sigma^N_{j=1} f^2_{oj})$ versus $(\text{sine}^2\theta)/\lambda^2$. Such a plot is called a Wilson plot. [29] The constant C was used in Equation II-B-8 to scale the relative structure factors to an absolute scale.

$$\ln\left[\frac{\overline{I_{rel}}}{\sum^N_{j=1} f^2_{oj}}\right] = \ln C - 2B(\text{sine}^2\theta)/\lambda^2 \qquad \text{II-B-6}$$

$$\overline{I_{abs}} = \sum^N_{j=1} f^2_{oj}\ e^{-2B(\text{sine}^2\theta)/\lambda^2} \qquad \text{II-B-7}$$

$$|F_{abs}| = \frac{|F_{rel}|}{\sqrt{C}} \qquad \text{II-B-8}$$

4. Phase Solution

a) The Direct Method

The direct method has been used with success for two structures reported in this Thesis and thus the three programs *NORMA*, *REL* and *RELFOR* are described herein. The subject has been adequately discussed[30-34] since the appearance of original papers by Sayre[35] and Hauptmann and Karle.[36]

The program *NORMA* treats the structure factors F_{hkl} from *PREP* according to Equation II-B-9. The normalized structure factors E_{hkl}[37] were so obtained. The term ε is an integer (usually 1) which is used to adjust for the degeneracy of the structure factors for reflections in symmetrical locations of reciprocal space. N is the total number of atoms in the cell and f_j is the atomic scattering factor for the jth atom at the 2θ value for the hkl reflection involved. The E values were normalized such that the average E^2 was 1. For this reason, reflections which were considered absent or statistically not significant were included.

$$E_{hkl} = \sqrt{\frac{|F_{hkl}|^2}{\varepsilon \sum_{j=1}^{N} f_j^2}} \qquad \text{II-B-9}$$

NORMA gives a summary of the number of E_{hkl} greater than 1.0, 2.0 and 3.0, respectively. Sayre's equation (II-B-10) states that the sign and magnitude of a reflection *hkl* is equal to the scaled (ϕ_{hkl}) sum of the products of all the pairs of structure factors whose indices add to give *hkl*. The two reflections and their sum constitute a triple. There are thus many such triples which must all be determined before Sayre's equation can be applied.

$$F_{hkl} = \phi_{hkl} \sum_{h'}\sum_{k'}\sum_{l'} \left[F_{h'k'l'} \cdot F_{h-h'\ k-k'\ l-l'}\right] \qquad \text{II-B-10}$$

The program *REL* computes all the triples for *NR* reflections with normalized structure factors (E_{hkl}) greater than a minimum value. Up to three seminvariant reflections (all of which must not possess even-even-even parity nor certain space group-dependent combinations of parities) were chosen from the *NR* reflections. Their E_{hkl}'s were given signs arbitrarily which subsequently remained fixed. These signed reflections define the origin.

N more reflections were chosen which must also not have all even parity. These reflections plus the seminvariants constitute the starting set. The starting set was chosen from the list of *NR* reflections according to a specific sorting order. The *N* reflections were given a sign for their E_{hkl}. Since all M reflections can be either positive or negative, there were thus 2^M combinations possible. The starting set was thus treated 2^M times by application of Equation II-B-11.

$$s(E_{hkl}) \sim s\left[\sum_{h'}\sum_{k'}\sum_{l'} E_{h'k'l'} \cdot E_{h-h'\ k-k'\ l-l'}\right] \qquad \text{II-B-11}$$

This abridged version of Sayre's equation states that the sign of the reflection hkl has a high probability (provided all three reflections are strong) of being determined by the product of the signs of reflections $h'k'l'$ and $h-h'$ $k-k'$ $l-l'$. A sorting order was specified such that Equation II-B-11 was applied to the starting set of reflections and the strongest ranking reflections first. The program expanded the set of phases which it either retained or discarded depending on their agreement with previously-determined phases. As more and more signs became determined, more terms entered into the summation and the requirement for higher intensity reflections lessened. The starting set, within any one of the 2^M tries, was not allowed to change.

The parameter *NBACK* determined the way the signs were treated. If *NBACK* was set equal to 0, as soon as a new sign was determined the reflections whose signs had not been determined earlier were re-examined in the first cycle. In subsequent cycles, the moment a new sign was determined it was used to determine new signs down the list until there were no more changes. If *NBACK* was set equal to 1, the new signs determined were not used to determine further signs until the first of the cycles was finished.

There is a formula (II-B-12) which assigns a probability *P* to the event that a sign has been correctly determined. This probability depends upon the magnitude of the normalized structure factors as well as the value *PROBK* which is approximately equal to $N^{-\frac{1}{2}}$ (where *N* is the number of atoms in the unit cell). *PROB1* is a minimum value for this aforementioned *P* below which the newly-determined sign will not be used in further phasing. *PROB2* is the minimum value of *P* for a phase to be considered determined in the output.

$$P = 0.5 + 0.5\tanh\left[\frac{1}{\sqrt{N}}\left(\left|E_{hkl} \cdot E_{h'k'l'} \cdot E_{h-h'k-k'l-l'}\right|\right)\right] \qquad \text{II-B-12}$$

The output from *REL* summarizes the phasing information for the treatment of *NR* reflections 2^N times. A table is printed which shows the number of cycles used for a run, the numbers of positive and negative reflections in the set and the consistency index C. This ratio is defined by Equation II-B-13 where < > means 'averaged over all hkl'.

$$C = \frac{\left\langle |E_{hkl}| \cdot \sum_{h'}\sum_{k'}\sum_{l'} E_{h'k'l'} \cdot E_{h-h'\ k-k'\ l-l'} \right\rangle}{\left\langle |E_{hkl}| \cdot \sum_{h'}\sum_{k'}\sum_{l'} |E_{h'k'l'}| \cdot |E_{h-h'k-k'l-l'}| \right\rangle}$$

In choosing the correct solution care was exercised to give high weight to the solutions which gave the highest consistency index, the minimum number of cycles and an equal number of pluses and minuses. The signs of the starting set should not have been predicted to be different from their starting signs during the iteration procedure for the true solution.

The output from *REL* for each set includes phased reflections. The program *RELFOR* prepares a Fourier input tape for the chosen set.

b) <u>The Fourier</u>

The structure factor F_{hkl} can be defined as the resultant of the X-rays scattered in the direction by the j atoms in the unit cell. The amplitude of the structure factor is determined both by the scattering factors for the individual atoms and by the phase δ. The phase is determined by the fractional co-ordinates of the atoms contributing to the reflection, the unit phase difference being 2π (Equation II-B-14). The magnitude of the structure factor is thus given by Equation II-B-15 where A_{hkl} and B_{hkl} are given in Equations II-B-16 and II-B-17, respectively.

$$\delta = 2\pi(hx + ky + lz) \qquad \text{II-B-14}$$

$$|F_{hkl}| = \sqrt{A_{hkl}^2 + B_{hkl}^2} \qquad \text{II-B-15}$$

$$A_{hkl} = \sum_j f_j \cos 2\pi(hx_j + ky_j + lz_j) \qquad \text{II-B-16}$$

$$B_{hkl} = \sum_j f_j \mathrm{sine}\, 2\pi(hx_j + ky_j + lz_j) \qquad \text{II-B-17}$$

Expressed in exponential form, the structure factor is given by Equation II-B-18 whereas the electron density $\rho(x,y,z)$ is expressed by Equation II-B-19.

$$F_{hkl} = \sum_j f_j \, e^{2\pi i(hx_j + ky_j + lz_j)} \qquad \text{II-B-18}$$

$$\rho(x,y,z) = \frac{1}{V}\sum_h\sum_k\sum_l F_{hkl} \, e^{-2\pi i(hx + ky + lz)} \qquad \text{II-B-19}$$

The coefficients F_{hkl} in the series shown in Equation II-B-19 constitute not only the magnitudes computed by *PREP* on the observed data but also have unobservable phases. F_{hkl} is actually a complex number which is the sum of A_{hkl} (Equation II-B-16) and iB_{hkl} (Equation II-B-17). For a centrosymmetric case, the term B_{hkl} is zero and the signed structure factor becomes simply A_{hkl}. Since this Thesis involves only centrosymmetric space groups, we shall restrict the discussion to this case.

Once a sufficient number of phases were assigned by direct or indirect methods, a Fourier[38-40] summation was computed based on the magnitude of the observed structure factors and the predicted signs. The Fourier program *FORDAP*[41] first expanded the data set to a triclinic from the higher symmetry it might have possessed. The electron density $\rho(x,y,z)$ was computed from a trignometric expansion of Equation II-B-19 where the coefficients of the Fourier series are known. Limits of x, y and z were set (usually to encompass an asymmetric unit only) and intervals were chosen to ensure a specific and sufficient resolution in angströms. The electron density was then calculated at each point in the cell and this was printed out as an integer value normalized to 999 as the largest sum.

The program *FORDAP* was also used to calculate a Patterson function.[42] For a Patterson, the coefficients used in the Fourier summation were the squares of the observed structure factors. There were thus no phases involved. *FORDAP* here again normalized the output to 999 as the largest vector sum. The function transformed is given in Equation II-B-20.

$$P(x,y,z) = \frac{1}{V}\sum_h\sum_k\sum_l |F_{hkl}|^2 \cos 2\pi(hx + ky + lz) \qquad \text{II-B-20}$$

The peaks $P(x,y,z)$ in a Patterson synthesis correspond to interatomic vectors. This information was used[43] to solve for the positions of the heavy atoms in the cell. The largest peak (999) was observed to be at the origin. There should be N^2-N vectors not on the origin (where N is the number of atoms in the cell). There was considerable overlap of peaks due to the diffuse character of the atoms in space. This was minimized by the so-called 'sharpened Patterson function'. Here, the scattering power of the atom is corrected for thermal motion and for its dependence on (sineθ)/λ. The squares of the sharpened structure factors, calculated from the squares of their observed counterparts using Equation II-B-21, were used.[44] B is the overall thermal parameter predicted by *PREP* and f_{oj} is the mean atomic scattering factor for the j^{th} atom. These squared structure factors were used in the Patterson synthesis according to Equation II-B-20.

$$(F_{\text{sharp}})^2_{hkl} = \frac{\left[0.1667 + (\text{sine}^2\theta)/\lambda^2\right]\left[F_{\text{obs}}\right]^2_{hkl}}{\left[\sum_{j=1}^{N} f_{oj}\right]^2 e^{-B(\text{sine}^2\theta)/\lambda^2}}$$

II-B-21

The intensity of a Patterson peak resulting from the vector between two atoms of atomic numbers Z_1 and Z_2 was 999 times the ratio $Z_1Z_2/\Sigma_{j=1}^{N} Z_j$ where N is the number of atoms in the unit cell.

Another useful function of *FORDAP* was the synthesis of a difference Fourier. Here the coefficients of the Fourier series are simply the quantities ($F_{obs} - F_{cal}$). F_{cal} represents the calculated structure factors based on some predetermined model. The difference Fourier is equivalent to an observed synthesis using the signs of F_{cal} and the magnitude of F_{obs} minus a calculated synthesis using the signs and the magnitudes of F_{cal}. The options of *FORDAP* included the possibility of introducing an artificial map maximum (*RMAX*) which could be made to correspond to a previous difference synthesis. The electron density of a difference Fourier is in units of $\Delta e\text{Å}^{-3}$.

5. Least Squares Refinement

The positions found for the atoms by either the heavy atom method or the direct method were used to create a model of the contents of the unit cell. The accuracy of this model was ascertained by calculating structure factors F_{hkl} based on this model and comparing them to those observed. The F_{hkl} are functions not only of the variables x, y and z but also of the isotropic or anisotropic thermal parameters. These last parameters correct the model for the vibration of atoms in space due to thermal motion.

In the isotropic case the vibration is spherical and B, the isothermal parameter, is related to the mean square amplitude of vibration $\overline{\mu^2}$ by the equation $B = 8\pi^2\overline{\mu^2}$. In the more elegant extreme, 6 anisotropic thermal parameters can be assigned to each atom which is now assumed to vibrate preferentially in certain directions. The expression for the anisotropic temperature factor involves the unit cell parameters and is related to the geometric description of an ellipsoid, thus the expression 'thermal ellipsoid. An alternate description of the anisotropic factor was used in computation and does not reflect the interrelationship of the true anisotropic parameters. The anisotropic structure factor was thus defined by Equation II-B-22.

$$F_{hkl} = \sum_j f_j e^{2\pi i(hx_j+ky_j+lz_j)} e^{-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})} \qquad \text{II-B-22}$$

The observed structure factors are known quantities and the calculated structure factors represent the model sought. Corrections must be made to the atomic scattering factors in the model in order to compensate for the fact that the electrons are not free in the molecules but are bound. The free electron scattering factor f_j must be corrected by a real ($\Delta f'$) and an imaginary ($i\Delta f''$) dispersion correction.

The function which was minimized in the least squares analysis[45] is represented in Equation II-B-23 where w_{hkl} is the weight of an observation and is equal to the reciprocal of *sigma*. *Sigma* has the value calculated in *PREP* and k is the scale factor which is applied to F_{cal}.

$$D = \sum_{hkl} w_{hkl} \left[|F_{obs}| - |kF_{cal}| \right]^2 \qquad \text{II-B-23}$$

The derivative of the expression with respect to each parameter was set to zero. The normal equations were expanded by a Taylor series expansion, neglecting terms higher than first power. The equations were solved in their array form by the program according to the matrix Equation II-B-24 where p_i is the i^{th} parameter. The inverse of matrix A was used in the form $x = A^{-1}v$ The x's are the shifts in the refined parameters which were added to the p_i's to obtain new parameters.

$$\begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \vdots & & \ddots & \vdots \\ a_{n1} & \cdots & & a_{nn} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix} = \begin{pmatrix} v_1 \\ v_2 \\ \vdots \\ v_n \end{pmatrix} \qquad \text{II-B-24}$$

$$a_{ij} = \sum_{hkl} w_{hkl} \frac{\partial |F_{cal}|_{hkl}}{\partial p_i} \cdot \frac{\partial |F_{cal}|_{hkl}}{\partial p_j} \qquad \text{II-B-25}$$

$$x_i = \Delta p_i \qquad \text{II-B-26}$$

$$v_i = \sum_{hkl} w_{hkl} (\Delta F_{hkl}) \cdot \frac{\partial |F_{cal}|_{hkl}}{\partial p_i} \qquad \text{II-B-27}$$

The modified version of *SFLS-5* used was a 'full-matrix' least squares program with the option of separating the matrix into several matrices (up to 9 in number). For the calculation of structure factors, the program does not expand the number of atoms in the asymmetric unit to the number in the unit cell. Rather it expands the indices using the input transformation matrices for the unit cell symmetry.

The estimated standard deviation of parameter p_i (σ_{pi}) was calculated from Equation II-B-28 where b_{ii} is the i^{th} diagonal element of the inverse matrix A^{-1}, w_{hkl} is the weight ($sigma^{-1}$) of the hkl structure factor difference ΔF_{hkl} ($|F_{obs}|_{hkl} - |F_{cal}|_{hkl}$), m is the number of observations and n is the number of parameters. The 'goodness of fit' parameter is defined by Equation II-B-29. It differs from II-B-28 in that it does not involve the diagonal element of the inverse matrix.

$$\sigma_{pi} = \sqrt{b_{ii}\left[\sum_{hkl} w_{hkl}\,\Delta F^2_{hkl}\right] \Big/ (m-n)} \qquad \text{II-B-28}$$

$$\sqrt{\left[\sum_{hkl} w_{hkl}\,\Delta F^2_{hkl}\right] \Big/ (m-n)} \qquad \text{II-B-29}$$

The discrepancy indices (residual or reliability factors) quoted are computed using Equations II-B-30 and II-B-31.

$$R = \frac{\sum_{hkl} \left||F_{obs}|_{hkl} - |F_{cal}|_{hkl}\right|}{\sum_{hkl} |F_{obs}|_{hkl}} \qquad \text{II-B-30}$$

$$R_w = \left(\frac{\sum_{hkl} w_{hkl} \left[|F_{obs}|_{hkl} - |F_{cal}|_{hkl} \right]^2}{\sum_{hkl} w_{hkl} \left[|F_{obs}|_{hkl} \right]^2} \right)^{\frac{1}{2}} \qquad \text{II-B-31}$$

The program *NUCLS4*[46] refines certain parts of a molecule as if it were a rigid body. Fewer parameters are thus needed in the refinement to achieve approximately the same result. For example, the 240 parameters necessary to refine isotropically the ten phenyl groups of di-μ-(bis-(diphenylarsino)methane)-μ-diphenylacetylenedicarbonyl-dicobalt(0) were reduced to 120 in the rigid body program. For a rigid phenyl group, *NUCLS4* uses three co-ordinate parameters, three orientation parameters for each group, and an isotropic parameter for each atom in the group.

For structure factor calculations the rigid group contributions are summed separately from non-rigid atomic contributions. The rigid group is summed as the contributions of its individual atoms. The least squares process is essentially similar to that in *SFLS-5* except that separation of matrices is not possible.

6. Interpretive Programs

UTILITY[47] was used to compute the various geometric consequences of the determined positional parameters. Thermal ellipsoids were analyzed also. The program first converted the positional fractional co-ordinates to orthogonalized co-ordinates and the bond lengths, angles *etc.* were computed using standard techniques.[48] The standard deviation of a bond length σ_l was computed using Equation II-B-32 where σ_{x_1} and σ_{x_2} are the estimated standard deviations in the x parameters of atoms 1 and 2 respectively and l is the bond length.

$$\sigma_l = \sqrt{(\sigma^2_{x_1}+\sigma^2_{x_2})\left(\frac{\Delta x}{l}\right)^2 + (\sigma^2_{y_1}+\sigma^2_{y_2})\left(\frac{\Delta y}{l}\right)^2 + (\sigma^2_{z_1}+\sigma^2_{z_2})\left(\frac{\Delta z}{l}\right)^2} \qquad \text{II-B-32}$$

The program *DRAFT*[49] prepares a plot of the molecule in 'ball-and-stick' form or with the other molecules in the unit cell (packing diagram). *'OTLIPS* prepares a plot of the thermal ellipsoids of the molecule. Both programs generate a series of instructions which are applied by the Hewlett Packard 2114A computer to a Complot X-Y plotter.

CHAPTER III. THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIS(HEXACARBONYLDICOBALT-π-ETHYNYL)ARSINE.

SECTION A. INTRODUCTION

1. Transition Metal Complexes with Group VB Donor Atoms

Considerable interest has been shown in recent years in the transition metal complexes of phosphines and arsines. An excellent review by Booth[50] covers the field to 1964. Research published in this area during the last ten years has been reviewed by Robinson[51] and others[52-54]. The monodentate tertiary phosphine and arsine derivatives of cobalt carbonyls are of immediate interest. Usually the phosphine or arsine is found to substitute for a carbonyl, bonding to the metal in a fashion similar to the leaving group. The phosphorus or arsenic atom acts as a σ donor and a π acceptor. This second feature is particularly strong in PF_3 and thus complexes containing this ligand are very similar to the carbonyl complexes from which they are derived.

Normally, only one carbonyl per metal atom can be substituted without disintegration of the metal cluster. It appears that clusters containing bridging carbonyl ligands retain these carbonyl bridges[55] when substitution occurs. Dicobaltoctacarbonyl is an exception to this generalization. Bis{(tri-n-butylphosphine)tricarbonylcobalt} has been shown by X-ray structure analysis to have a non-bridged configuration with a linear P-Co-Co-P skeleton.[56] This skeleton forms a three-fold axis and there exists a crystallographic center of symmetry between the two cobalt atoms. The Co-Co bond length is 2.665(14)Å and the Co-P distance is 2.178(15)Å.

2. π Bonded Acetylenic Cobalt Carbonyls

Many reviews have been published on π bonded olefinic and acetylenic derivatives of transition metal carbonyls.[4,57-63] For the purposes of this Thesis, it was considered appropriate to survey the complexes of acetylenic cobalt carbonyls that have been reported with special emphasis on their structure and bonding.

The first report of an acetylenic dicobalthexacarbonyl occurred in 1954[64] with the publication of a note by Sternberg *et al.* It was discovered that the two bridging carbonyls in dicobaltoctacarbonyl ($Co_2(CO)_8$) could be replaced by an acetylenic moiety (R–C≡C–R'). The reaction was quantitative with the observed loss of 2 moles of carbon monoxide. The substituents on the acetylene in the complexes prepared were phenyl, C_5H_{11}, C_2H_5, CH_2OH and hydrogen. All compounds were deeply coloured crystalline solids with the exception of $Co_2(CO)_6(HC{\equiv}CH)$ which was a dark red oil. A brief discussion of the possible geometries of the complex concluded that it was reasonable to assume the C-C bond was parallel to the Co-Co bond. Allowance was also made for the possibility that the C-C bond was perpendicular to the Co-Co bond, but not in the same plane. A complete paper, published subsequently, reaffirmed these conclusions.[65] It was stated that X-ray analysis would be necessary to settle this question.

An initial study of the kinetics of the acetylene-dicobaltoctacarbonyl reaction was undertaken.[66] From a mathematical analysis of the kinetic data of the reaction of dicobaltoctacarbonyl with hex-1-yne and hex-2-yne, a reaction mechanism was proposed. It was concluded that in solution, $Co_2(CO)_8$ is in equilibrium with a reactive species which is less stable than itself. This reactive species was postulated as being one in which the cobalt-cobalt bond was broken homogeneously. The acetylene then was claimed to substitute for one carbonyl giving an acetylene dicobaltheptacarbonyl intermediate which subsequently decomposed to the acetylene dicobalthexacarbonyl complex.

The same authors also reported [67] a study of the relative reaction rates of formation of a series of substituted acetylene dicobalthexacarbonyl complexes. The amount of carbon monoxide liberated was recorded as a function of time and the half-life of the reaction was used as a basis for comparison. The authors found that no clear correlation existed between steric or electronic factors and reaction rate. If any factor was significant, it was steric rather than electronic. The reaction rates were not appreciably different at the outset.

Recently, Ellgen [68] has disproved the reaction mechanism proposed earlier for the formation of these compounds. The existence of a reactive form is not implied by a parallel study on the formation of tetracobaltdodecacarbonyl from $Co_2(CO)_8$. By extrapolation, the authors show (with newly-collected data) that a mechanism involving the dissociation of $Co_2(CO)_8$ to $Co_2(CO)_7$ with subsequent attack by acetylene and liberation of another mole of CO is more likely. The rate-determining step is the first one which explains why the relative rate study was so unsuccessful.

Extensive studies of the infrared spectrum of these compounds have been undertaken. The first such study was that of G. Bor.[69] Here, only a cursory analysis of the spectrum was given. The appearance of five terminal stretching carbonyl bands confirmed the structure as consisting of mutually perpendicular C-C and Co-Co bonds in different planes. Recently, more thorough analyses, coupled with nuclear magnetic resonance (nmr) data, have permitted a considerable fund of knowledge to be accumulated on the nature of the bonding in these complexes. Iwashita *et al.* published a paper [70] in which they assigned the infrared absorption bands for $(HC{\equiv}CH)Co_2(CO)_6$ unequivocally using isotopically-labelled molecules. The terminal C-O stretching vibrations were recorded as 2097.8, 2058.5, 2033.7, 2028.1 and 2016.6 cm^{-1}. The frequency of the C≡C stretching vibration was found to be 1402.5 cm^{-1} as compared to 1973.8 cm^{-1} [71] for pure acetylene. There is obviously a large change in the acetylenic bond upon complexation and this is ascribed to a change from a linear bent to a *cis*-bent configuration. A parallel was found in the infrared spectrum of the first electronically-excited state of acetylene [72] which is *trans*-bent. For steric reasons, a *cis*-bent structure was preferred for the complexed acetylene. A normal co-ordinate analysis on the $(HC{\equiv}CH)Co_2$ portion of $(HC{\equiv}CH)Co_2(CO)_6$ [73] has shown this to be the most likely possibility. Bond formation has the effect of taking the electron from the highest bonding π orbital of the ligand to the lowest π^* orbital.

The hybridization of the acetylenic carbons from sp to approximately sp^2 upon complexation is shown by the nmr studies of Iwashita.[74] These studies were conducted on the methylacetylene and dimethylacetylene derivatives. Mass spectrometric analysis[75] of $(CF_3C{\equiv}CH)Co_2(CO)_6$ shows that the complex loses the six carbonyls to give $(CF_3C{\equiv}CH)Co_2^+$ which then progressively loses portions of the acetylenic moiety. A full fragmentation scheme is proposed. Another paper[76] showed that the formation of the diphenylacetylenedicobalthexacarbonyl complex is electrochemically irreversible.

In 1959, W.G. Sly[77] published preliminary results of an X-ray crystal structure analysis of the complex diphenylacetylenehexacarbonyldicobalt. The monoclinic crystal (Cc) gave 970 reflections and isotropic refinement was effected to a reliability index of 16%. Co-ordination about each cobalt atom was observed to be six-fold giving rise to a distorted octahedral configuration. The molecule is illustrated in Figure III-A-1 and the numbering scheme shown is that used in Table III-A-1 which gives the bond lengths and angles for the structure. It will be noted that the C-C distance was first quoted as 1.46Å but this was subsequently changed to 1.369Å with further refinement.[78]

The Co-Co bond makes an angle of 88° with the C-C bond of the acetylene. This is, by modern standards, a very inaccurate structure and, for purposes of comparison,

Figure III-A-1. The molecular configuration of μ-(diphenyl-acetylene)hexacarbonyldicobalt.

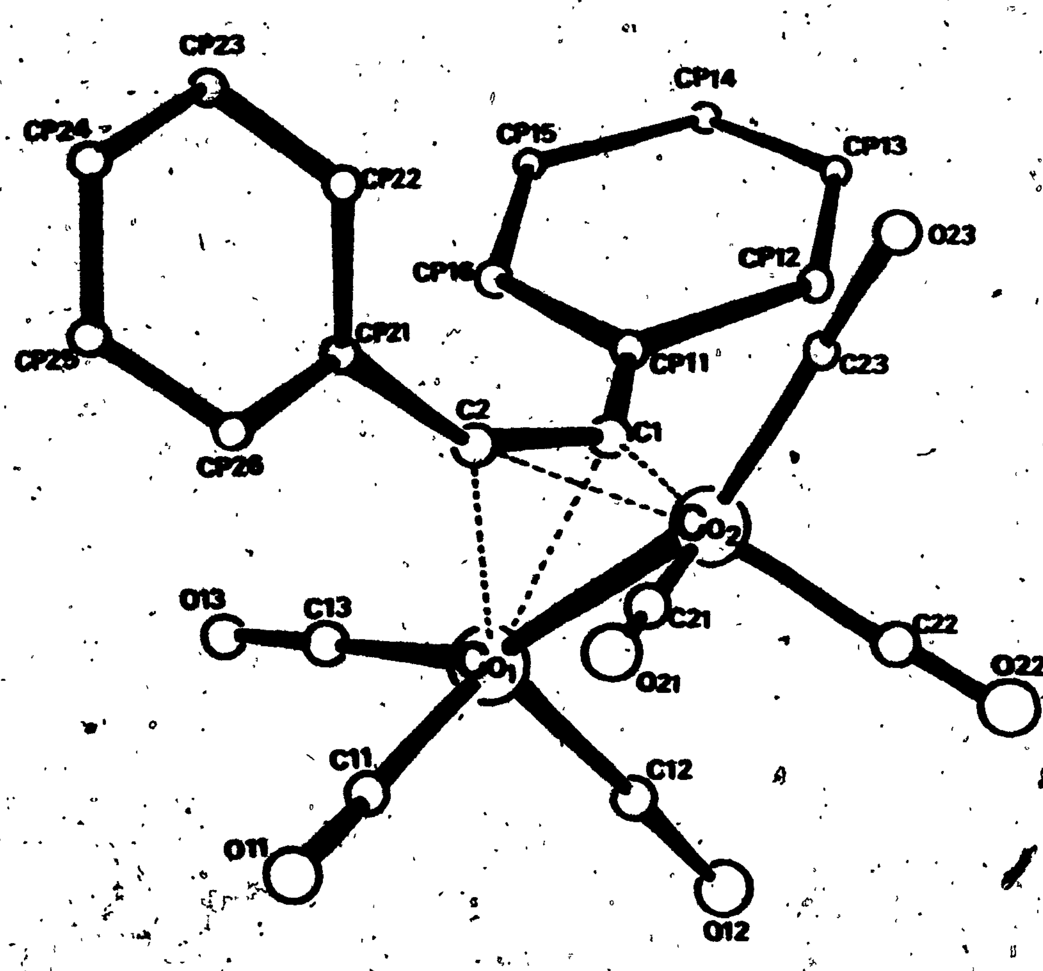

CP23
CP24
CP22
CP14
CP15
CP13
O23
CP16
CP12
CP21
CP25
CP11
C23
C2
C1
CP26
Co2
O13
C13
C21
C22
Co1
O21
O22
C11
C12
O11
O12

TABLE III-A-1

BOND LENGTHS (Å) AND SOME IMPORTANT BOND ANGLES (°) IN THE COMPLEX μ-(DIPHENYLACETYLENE) HEXACARBONYLDICOBALT

Co1 -Co2 :	2.47	C1 -C2 :	1.46/1.369
Co1 -C1 :	2.02	Co2 -C2 :	1.93
Co1 -C2 :	2.01	Co2 -C1 :	1.89
Co1 -C11 :	1.79	Co2 -C21 :	1.71
Co1 -C12 :	1.76	Co2 -C22 :	1.80
Co1 -C13 :	1.71	Co2 -C23 :	1.72
C11 -O11 :	1.21	C21 -O21 :	1.22
C12 -O12 :	1.23	C22 -O22 :	1.22
C13 -O13 :	1.25	C23 -O23 :	1.26
C1 -CP11:	1.43	C2 -CP21:	1.42
CP11-CP12:	1.48	CP21-CP22:	1.40
CP12-CP13:	1.49	CP22-CP23:	1.43
CP13-CP14:	1.32	CP23-CP24:	1.41
CP14-CP15:	1.37	CP24-CP25:	1.38
CP15-CP16:	1.54	CP25-CP26:	1.46
CP16-CP11:	1.42	CP26-CP21:	1.45
Co1 -C2 -Co2 :	77	Co1 -C1 -Co2 :	78
C1 -Co1 -C2 :	43	C1 -Co2 -C2 :	45
Co2 -Co1 -C11 :	103	Co1 -Co2 -C21 :	100
Co2 -Co1 -C12 :	99	Co1 -Co2 -C22 :	96
C2 -Co1 -C13 :	104	C2 -Co2 -C23 :	103
C1 -Co1 -C13 :	100	C1 -Co2 -C23 :	95
CP21-C2 -C1 :	137	CP11-C1 -C2 :	139

the results must be approached with considerable skepticism. Indeed, if the six bond lengths in one phenyl ring can vary from 1.32 to 1.54Å, what confidence can be shown for the rest of the bond distances and angles quoted? It is regrettable that Sly never completed his work on this complex.

The structure can safely be evaluated from two geometric points of view. First, the cobalt atom can be considered to be approximately in the d^2sp^3 hybridized state and thus the acetylenic carbons would be approximately tetrahedral (sp^3). This is not compatible with a C-C distance of 1.369Å for the acetylenic bond. The second possibility is that each cobalt atom is trigonal bipyramidal (dsp^3) and one of the hybrid orbitals is directed towards the center of the acetylene C-C bond.

The bonding of acetylene to the dicobalt-hexacarbonyl fragment is similar to the bonding of olefins discussed in the early 1950's by Dewar [79] and Chatt and Duncanson. [80] A σ-type bond is formed between the filled π bonding molecular orbital of acetylene and an empty metal hybrid orbital. At the same time, a π type of bond is also formed between the filled dπ type orbital of the metal and the empty pπ* orbital of acetylene. This synergistic bonding scheme is similar in concept to that proposed for the bonding of carbonyls and phosphines.

Brown [78] has studied the metal-metal bonding in μ-(diphenylacetylene)hexacarbonyldicobalt by applying 'simple' molecular orbital theory to the complex in its trigonal bipyramidal hybridized state. The metal-metal bond occurs by direct overlap of the 4p orbitals of the cobalt atoms. Blizzard and Santry [81] have reported a study of a model in which the principal consideration has been interactions within an isolated acetylene molecule. Addition of electron density to the π^* orbital of acetylene would lead to a *cis*- or *trans*-bent structure with *cis*-bent being slightly preferred. *Trans*-bending was also shown to lead to a weakening of the metal-acetylene bond whereas *cis*-bending did not affect this bond. R. Mason has recently reviewed the currently accepted bonding theories of acetylenic-dicobalthexacarbonyl complexes.[82]

A vast series of substituted acetylenic hexacarbonyldicobalt complexes have been synthesized to date. The preparation and some chemical reactions of ditertiarybutylacetylenehexacarbonyldicobalt have been reported.[83] A series of trifluoromethyl and perfluorophenyl substituted acetylenes have also been prepared and studied.[84-92] Also prepared was the dicyanoacetylene complex[93] as well as a series of complexes of alcoholic acetylenes[94-97] and carboxylic acid acetylenes.[98]

Many unusual complexes have also been reported. Typical of these are the diferrocenylacetylenehexacarbonyldicobalt[99] and the tri(phosphonitrilicfluoride)phenylacetylene-hexacarbonyldicobalt [100] complexes. Some bis-complexes of diacetylenes have also been synthesized[101-102] as well as a complex $R_2M(C{\equiv}CR'{\cdot}Co_2(CO)_6)_2$ where R is silicon, germanium or tin.[103]

Hexacarbonyldicobalt fragments have been used as effective blocking groups. Complexation of selective acetylenic linkages with $Co_2(CO)_6$ has allowed other similar bonds of the same organic molecule to be preferentially treated.[104] Friedel-Crafts alkylation of the rings in free diphenylacetylene is impossible under normal circumstances. However, when the acetylene moiety is complexed to a $Co_2(CO)_6$ unit, the alkylation reaction is possible due to the activation of sites *para-* to the substituted acetylene position towards electrophilic substitution.[105] The alkylated diphenylacetylene can subsequently be removed from the cobalt carbonyl fragment.

The study of substitution reactions of acetylenic dicobalthexacarbonyls has been undertaken in this laboratory to determine the degree of substitution possible and the effect of such substitution on the acetylenic moiety. Other researchers have been involved in the same problem.[106-107]

Complexes containing the $Co_3(CO)_9C$ fragment have been extensively studied by Penfold.[108] Some of these structures contain an acetylenic linkage which has been complexed with a $Co_2(CO)_6$ unit. X-ray crystallographic studies of two such complexes affords a greater insight into the nature of this type of bonding.

The reaction of chloromethinylenneacarbonyltricobalt ($ClCCo_3(CO)_9$) with mesitylene[109] has given a number of side products including a complex formulated as $Co_5(CO)_{15}C_3H$. An X-ray crystallographic structure analysis of this complex was undertaken by Dellaca *et al.*[110] The complex consists of a $Co_3(CO)_9C$ tetrahedron linked, through the methinyl carbon atom, to an acetylenic moiety. The acetylene is bonded to a $Co_2(CO)_6$ fragment, whence the interest in this structure in this Introduction. The compound crystallizes in space group $P\bar{1}$ and refinement based on 1392 reflections gave an isotropic discrepancy factor of 6.7%. Using the numbering scheme given in Figure III-A-1 for the acetylenic-$Co_2(CO)_6$ part of the molecule (ring 1 of the $(PhC{\equiv}CPh)Co_2(CO)_6$ complex is replaced by a hydrogen whereas ring 2 is substituted for the methinylenneacarbonyltricobalt moiety), the bond distances and angles are given in Table III-A-2.

Another similar structure is that of hexacarbontetracosacarbonyloctacobalt ($Co_8(CO)_{24}C_6$). In this

TABLE III-A-2

BOND LENGTHS (Å) AND SOME IMPORTANT BOND ANGLES (°) FOR THE ACETYLENIC - $Co_2(CO)_6$ MOIETY IN TRICARBONPENTADECACARBONYLPENTACOBALT AND IN HEXACARBONTETRACOSACARBONYLOCTACOBALT.

Distance or angle	Tricarbonpentadecacarbonylpentacobalt	Hexacarbontetracosacarbonyloctacobalt Seyferth[111]	Hexacarbontetracosacarbonyloctacobalt Dellaca[112]
Co1-Co2	2.447(4)	2.469(6)	2.461(8)
C1 -C2	1.34(2)	1.37(4)	1.37(3)
Co1-C1	1.95(1)	1.99(3)	1.96(3)
Co2-C2	1.94(2)	2.02(3)	1.95(3)
Co1-C2	1.99(2)	2.01(3)	1.97(3)
Co2-C1	2.01(2)	1.96(3)	1.95(3)
Co1-C11	1.81(2)	1.79(4)	1.76(4)
Co1-C12	1.77(2)	1.88(4)	1.75(5)
Co1-C13	1.75(2)	1.84(4)	1.72(4)
Co2-C21	1.80(2)	1.74(4)	1.75(4)
Co2-C22	1.78(2)	2.00(5)	1.80(4)
Co2-C23	1.75(2)	1.77(3)	1.77(4)
C-O(carbonyl)	1.17(2)	1.15(5)	1.16(3)
Co1-C2 -Co2	76.5(5)	75(1)	78(1)
Co1-C1 -Co2	79.2(6)	77(1)	78(1)
C1 -Co1-C2	39.9(6)	40(1)	41(1)
C1 -Co2-C2	39.7(6)	40(1)	41(1)
Co2-Co1-C11	102.8(6)	98(1)	101(1)
Co1-Co2-C21	101.6(5)	96(2)	101(1)
Co2-Co1-C12	98.1(6)	101(1)	100(1)
Co1-Co2-C22	97.8(7)	101(2)	97(1)
Co2-Co1-C13	147.6(6)	151(1)	148(1)
Co1-Co2-C23	148.1(7)	150(2)	149(1)
C2 -Co1-C13	102.6(8)	101(2)	101(1)
C2 -Co2-C23	103.6(8)	100(1)	104(1)
C1 -Co1-C13	97.5(8)	103(2)	99(1)

TABLE III-A-2 (CONT'D)

C1 -Co2-C23	97.8(8)	101(2)	98(1)
C1 -C2 -(CP21)	145.6(14)	140(3)	138(2)
C2 -C1 -(CP11)	-----	148(3)	142(2)

complex, two methinylenneacarbonyltricobalt fragments are linked by a four carbon skeleton containing two acetylenic bonds. One of these acetylenic bonds is co-ordinated to a $Co_2(CO)_6$ unit whereas the other is uncomplexed. This structure is unique in that the bond distances for both co-ordinated (1.367(42)Å) and non-co-ordinated (1.199(43)Å) acetylene can be compared directly. The X-ray crystallographic structure determination of the benzene hemisolvate was published by Seyferth *et al.*[111] Subsequently, the unsolvated structure was reported by Dellaca and Penfold.[112] Bond lengths and angles of the acetylenic hexacarbonyldicobalt unit are given in Table III-A-2 for both independent structure determinations. The numbering scheme used is again as in Figure III-A-1 except that the $-C{\equiv}C-CCo_3(CO)_9$ unit replaces ring 1 and ring 2 is again replaced by methinylenneacarbonyltricobalt.

The compound octafluorocyclohexa-1,3-diene was reported[113] to react with dicobaltoctacarbonyl to form a compound with stoichiometry $C_6F_6Co_2(CO)_6$. A preliminary report[114] of the X-ray crystallographic structure determination showed that the C_6F_6 unit (perfluorocyclohex-1-yn-3-ene) was bonded through the triple bond to the $Co_2(CO)_6$ fragment just as diphenylacetylene is bonded to $Co_2(CO)_6$ in diphenylacetylenehexacarbonyldicobalt. A more complete publication of this structural analysis appeared in 1968.[115] The molecule crystallizes in space group $P2_1/c$ and 936 independent reflections were collected. Anisotropic least squares refinement to a residual index of 7.8% gave the bond distances and angles listed in Table III-A-3. The molecule is illustrated in Figure III-A-2.

In this molecule, the fluorine atoms increase the extent of 'back-donation' to the acetylene thus accounting for the stability of the complex. The angles at the acetylenic carbons are constrained to be around 120° whereas those in the other acetylenic dicobalthexacarbonyls are *circa* 140°. This does not appear to greatly affect the bonding. Roe and Massey [116] have recently published a report on the preparation of a $Co_4(CO)_{10}$ derivative of the above perfluoroorganic ligand using perfluorobenzene magnesium bromide and dicobaltoctacarbonyl. Studies by mass spectrometry and infrared spectroscopy have shown it to be similar to the diethylacetylenedecacarbonyltetracobalt cluster reported by Dahl and Smith. [117]

In this structure, the $Co_4(CO)_{10}$ unit is described as a 'butterfly form' and the largest Co–Co distance so formed is spanned by the acetylene. The acetylenic C≡C distance is 1.44(2)Å. This value should not be related to the other structures reported in the Introduction since the bonding in this complex is not the same.

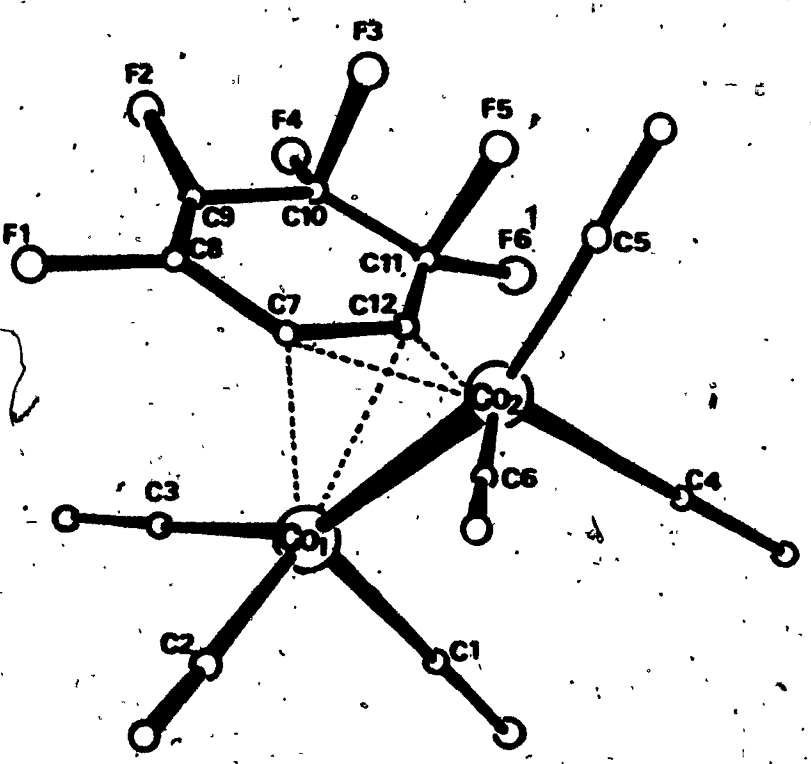
TABLE III-A-3

BOND LENGTHS (Å) AND SOME BOND ANGLES (°) IN PERFLUOROCYCLOHEX-1-YN -3-ENEHEXACARBONYLDICOBALT

Co1-Co2	2.488(4)	C7 -C12	1.36(3)
Co1-C12	1.91(2)	Co2-C7	1.93(2)
Co1-C7	1.90(2)	Co2-C12	1.96(2)
Co1-C2	1.72(3)	Co2-C6	1.80(2)
Co1-C1	1.87(2)	Co2-C4	1.84(2)
Co1-C3	1.86(3)	Co2-C5	1.80(2)
C-O(carbonyl)	1.13(3)		

Co2-Co1-C2	100(1)	Co1-Co2-C6	100(1)
Co2-Co1-C1	101(1)	Co1-Co2-C4	100(1)
Co2-Co1-C3	150(1)	Co1-Co2-C5	146(1)
C8 -C7 -C12	119(2)	C11-C12-C7	123(2)

Figure III-A-2. The molecular configuration of perfluorocyclohex-1-yn -3-enehexacarbonyldicobalt.


F3
F2
F4
F5
F1
C9
C10
C8
C11
F6
C5
C7
C12
Co2
C6
C3
C4
Co1
C2
C1

3. π *versus* σ Bonding in Hexacarbonyldicobalt Ethynyl Complexes of Phosphorus and Arsenic.

It has been seen that phosphines and arsines bond to dicobaltoctacarbonyl using their lone pair of electrons to form a σ bond. It has also been discussed, at some length, how acetylenic-dicobalthexacarbonyl linkages form and the nature of the bonding involved. Molecules with both bonding possibilities are of interest in that a study of such patterns that may develop might give important information on the affinity of dicobaltoctacarbonyl for either σ or π bonding, or both. Such a study was the original goal of the work reported in this Chapter and, although its scope was greatly reduced due to the formation of polymers and intractable products, important information concerning the competitive nature of the σ and π bond potential of triethynylarsine for dicobaltoctacarbonyl was gleaned.

A parallel study has been conducted by A.J. Carty[118] on the reactions of dicobaltoctacarbonyl with phosphinoacetylenes, R'PC≡CR". An original paper[119] was published on the reaction of $Co_2(CO)_8$ with bis(diphenylphosphino)acetylene ($Ph_2PC{\equiv}CPPh_2$). The acetylene did not π bond but both phosphines bonded σ to form a bridge between two $Co_2(CO)_7$ fragments. These moieties retained the bridging carbonyl structure of $Co_2(CO)_8$. When the ligand

$Ph_2PC{\equiv}CCF_3$ was used, a complex involving both σ bonding of the phosphorus atom and π bonding of the acetylene moiety was obtained. The molecule $Co_4(CO)_{10}(Ph_2PC{\equiv}CCF_3)_2$[120] was shown by X-ray crystallographic structure determination to consist of two $Co_2(CO)_5$ units linked by the two $Ph_2PC{\equiv}CCF_3$ moieties both by π acetylenic and σ donor bonding. The Co–Co bond lengths averaged 2.473Å and the C–C bonds of the 'acetylenic bonds' averaged 1.348Å. It was also observed that the Co–C(carbonyl) bond *trans* to the Co–Co bond was shorter (1.751Å) than the remaining Co–C(carbonyl) bonds (average 1.826Å).

SECTION B: EXPERIMENTAL

1. Synthesis and Characterization of Triethynylarsine

With modifications, the preparation of triethynylarsine was effected as described by Voskuil and Arens.[121] Preparation of the ethynylmagnesium bromide precursor was adapted from a procedure by Skattebol, Jones and Whiting.[122]

To 50 ml of tetrahydrofuran (C_4H_8O), which had been refluxed under nitrogen for four days in the presence of lithium aluminum hydride and then distilled, was added 2.4 g (0.1 gram atom) of magnesium metal turnings. This was done in a 500 ml three-necked flask fitted with a reflux condenser (with a nitrogen gas inlet-outlet tube protected with a calcium chloride drying tube), a thermometer (-20^{o} to 150^{o}C) and a pressure-equalized dropping funnel which contained a solution of 8.2 ml (11.97 g, 0.11 moles) bromoethane (C_2H_5Br) in 85 ml tetrahydrofuran.

The apparatus was flushed with dry nitrogen gas. The Mg turnings and tetrahydrofuran were stirred with a magnetic stirrer and heated to 35^{o}C. Then 10 ml of the bromoethane solution were added while stirring vigorously and the temperature rose to 55^{o}C. The flow rate of addition of bromoethane was adjusted to maintain this temperature to within 5^{o}C. The solution turned black as the reaction (III-B-1) proceeded. When all the bromoethane was added, the mixture was stirred at 45^{o}C for an additional hour. The solution of ethylmagnesium bromide so formed was stored at room temperature in a pressure-equalized dropping funnel.

$$Mg + CH_3CH_2Br \xrightarrow{C_4H_8O} CH_3CH_2MgBr \qquad \text{III-B-1}$$

A 500 ml three-necked round bottom flask was fitted with a reflux condenser as above, a pressure-equalized dropping funnel containing the ethylmagnesium bromide and a rubber stopper with an acetylene gas inlet tube that reached under the surface of 100 ml of dry oxygen-free tetrahydrofuran. The acetylene gas was purified by passing it from its 250 p.s.i. tank through concentrated sulphuric acid using a gas bubbler. It was then passed through a trap maintained at -75^{o}C (care was exercised to maintain the temperature above -81^{o}C, the normal boiling point of acetylene) and allowed to bubble in to the tetrahydrofuran so as to saturate it.

A few drops of the Grignard reagent were added to the acetylene-tetrahydrofuran solution and the liquid took on a pink colour which became progressively darker as the reaction (III-B-2) proceeded. Much frothing was observed as the ethane was liberated. The Grignard was added dropwise to ensure an even temperature. It also ensured a continual excess of acetylene gas which was bubbled through the solution rather vigorously. The solution was allowed to stir an additional 30 minutes with slowly-bubbling acetylene to ensure complete reaction. The solution was indeed observed to be inhomogeneous at room temperature and it was stored in a pressure-equalized dropping funnel at 30°C until used in the final step.

$$CH_3CH_2MgBr + HC{\equiv}CH \xrightarrow{C_4H_8O} HC{\equiv}CMgBr + C_2H_6\uparrow$$

III-B-2

A 500 ml three-necked flask was fitted with a reflux condenser as above, an alcohol thermometer (-100 to 50°C) and a pressure-equalized dropping funnel containing the ethynylmagnesium bromide solution. In the three-necked flask was placed 2.8 ml arsenic trichloride (6.06 g, 0.033 moles) in 40 ml diethylether (distilled under nitrogen after refluxing for one day over calcium hydride). This solution was cooled in an acetone-dry ice bath to -30°C and a few drops of the Grignard were added. The clear solution turned milky and the temperature rose slightly. The flow rate was adjusted to maintain -30°C in the acetone-dry ice bath. Care was taken not to go below -30°C because the reaction mixture would become too viscous to stir properly.

$$AsCl_3 + 3HC{\equiv}CMgBr \longrightarrow As(C{\equiv}CH)_3 + 3MgBrCl$$

III-B-3

When all the Grignard had been added, the reaction mixture was allowed to reach room temperature and stirred at this temperature for one full hour. Then the beige mixture was cooled to $-20^{o}C$ and 50 ml of a 10% w/w solution of ammonium chloride (NH_4Cl) in water was added at a rate to maintain the temperature of the stirred mixture at about $-20^{o}C$. The mixture was once again allowed to reach room temperature. It was then placed in a separatory funnel where the clear top organic layer was saved and, after washing twice with diethylether, the bottom aqueous layer was discarded.

About 10 cm^3 of molecular sieve, type 4A in 1/16th inch pellets (Fisher Scientific Company), were added to the combined organic fractions and this was left for 20 hours at room temperature in a stoppered flask. (By this time a respite was needed from the rather overwhelming odour of triethynylarsine: that of geraniums).

The organic solution of triethynylarsine was placed on the rotary evaporator. The solution was reduced from a volume of 200 ml to a volume of 10 ml to produce a viscous brown liquid. The flask was stoppered and transferred to a vacuum line. A system, consisting of (A) the round bottom flask containing the 10 cm^3 of crude product solution, (B) a flow-through U-shaped tube, (C) another flow-through U-shaped tube and (D) a round bottom 50 ml flask which could be sealed, was evacuated while maintaining flask A at the temperature of liquid nitrogen.

The first trap (B) was cooled in a methanol-ice bath to a temperature within the range -25°C to -20°C. The second trap (C) was cooled to -78°C in an acetone-dry ice bath. On warming the crude mixture to room temperature, the remaining tetrahydrofuran distilled through the first trap and condensed in the second. The crystalline triethynylarsine condensed in the first trap. The volatility of the product was such that heating of the crude product was unwarranted thus eliminating unnecessary decomposition and taming the unusually high propensity of these compounds to explode when subjected to heat. The solid salt-like crystals were transferred to storage flask D and stoppered therein. The ligand, now in its pure form, was stored in the refrigerator until needed.

The theoretical yield of triethynylarsine was 0.033 moles or 4.95 g. A total of 3.61 g was obtained representing a 73% yield.

The colourless and malodourous crystals obtained melted in the range 48→50°C (49→50°C[121]). The infrared spectrum was recorded on the Perkin Elmer IR-457 in nujol mull form. The spectrum was calibrated using a polystyrene film. Peaks at 3295(vs), 2044(m), 1292(w), 681(s), 651(s) and 516(m) cm^{-1} agree with those reported by Voskuil and Arens [121] as well as Miller and Lemmon.[123]

The proton magnetic resonance (pmr) spectrum was recorded. A 10% (w/v) solution of the product in dichloromethane gave one singlet at δ = 2.72 ppm. This compares favourably with δ = 2.62 ppm[121] recorded earlier.

2. The Synthesis and Characterization of Tris(hexacarbonyl-dicobalt-π-ethynyl)arsine

Dicobaltoctacarbonyl ($Co_2(CO)_8$ - 0.551 g, 1.52 millimoles) was dissolved in 25 ml of cyclohexane (C_6H_{12}), previously dried by refluxing under nitrogen gas with calcium hydride for a week and then distilled. Triethynylarsine (0.063 g, 0.42 millimoles) was dissolved in an additional 25 ml of cyclohexane. The first solution was added to the second.

There was immediate evolution of a gas and the reaction mixture turned from brown-yellow, characteristic of dicobaltoctacarbonyl in solution, to deep red during the two hour period the reaction mixture was stirred. No further evolution of gas was observed at this time. The solution was placed on the rotary evaporator and the solvent was removed *in vacuo* to a volume of 4 ml.

A chromatographic column was prepared. The column was 1 inch in diameter and 12 inches long. The silica gel was deactivated with 13% (w/w) water and mixed with cyclohexane. The column was packed wet and the 4 ml of solution were placed on it. Two bands were observed upon elution with cyclohexane. The first, and by far the largest, was collected and the cyclohexane was completely removed *in vacuo*. The yield was 0.391 g or 93%. The product was then redissolved in 15 ml cyclohexane and the solution was placed in the refrigerator (at 0°C) overnight.

The second band was collected, the solvent evaporated, and the small amount of solid obtained was dried *in vacuo*. An infrared spectrum identified this solid as the starting material dicobaltoctacarbonyl when compared to the literature spectrum.[12] There had been no detectable odour characteristic of the arsine in the reaction mixture.

The refrigerated solution of product was observed to deposit small deep red crystals which had the external appearance of truncated octahedra. These crystals were isolated by filtration and washed several times with cold cyclohexane. They were dried *in vacuo* for 24 hours.

The complex decomposed without melting in the temperature range 119°C→124°C. An unidentified black powder resulted. The complex was soluble in polar as well as non-polar solvents being relatively stable in air but somewhat less so in solution. For tris(hexacarbonyldicobalt-π-ethynyl)arsine ($C_{24}H_3AsCo_2O_{18}$), the theoretical elemental analysis gives %C = 28.60, %H = 0.30, %As = 7.43 and %Co = 35.09. The experimentally-determined chemical analysis gave %C = 28.80, %H = 0.32, %As = 7.32 and %Co = 35.01.

The infrared spectrum of tris(hexacarbonyl-dicobalt-π-ethynyl)arsine is reported in Table III-B-1. The 2000 to 2100 cm^{-1} region of the infrared spectrum as recorded in carbon disulphide solution is shown in Figure III-B-1. The Perkin Elmer IR-457 was used to record this spectrum.

The nmr spectrum was recorded using a 20% (w/v) dichloromethane solution. Although the peak was of low intensity, a singlet was nevertheless recorded at δ = 6.3 ppm. The complex was not sufficiently volatile to obtain a mass spectrometric analysis.

TABLE III-B-1

INFRARED PEAKS[a] FOR TRIS(HEXACARBONYLDICOBALT-π-ETHYNYL)ARSINE

3118(w)[b]		861(w)
2971(w)[b]		770(w)
2090(vs)	2090(s)[c]	
2068(s)	2068(vs)[c]	569(w)
2036(s)	2058(w,sh)[c]	523(m)
2021(vs)	2029(vs)[c]	515(m,sh)
2007(vs)	1986(w)[c]	494(m)
1986(w)		453(w)
		384(m,bd)
1438(w)[b]		360(m)
1418(w)[b]		

a Unless otherwise indicated, all frequencies are quoted in cm^{-1} in the form of their nujol mulls on KBr windows using the IR-225 ($\pm 1cm^{-1}$).

b Recorded by IR-457 ($\pm 3cm^{-1}$) of a tetrachloroethylene solution using 1.0 mm sodium chloride matched cells.

c Recorded by IR-457 ($\pm 3cm^{-1}$) of a carbon disulphide solution using 1.0 mm sodium chloride matched cells.

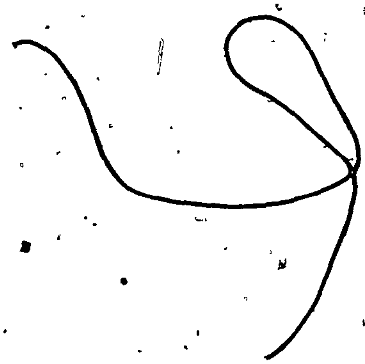
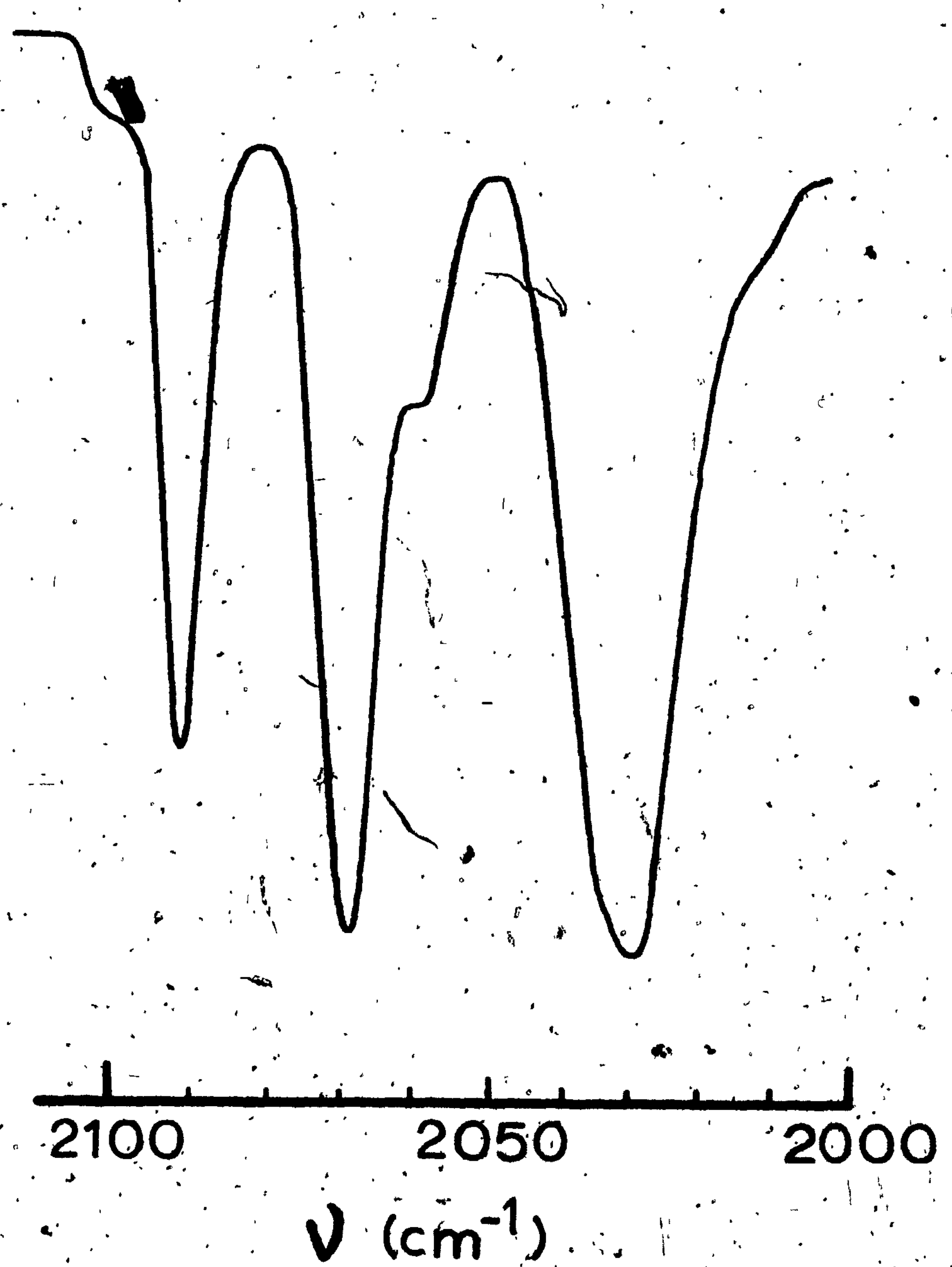


Figure III-B-1. The infrared spectrum of tris(hexacarbonyl-dicobalt-π-ethynyl)arsine from 2000 to 2100 cm^{-1} showing terminal carbonyl C-O stretching peaks in carbon disulphide solution.


2100
2050
2000
ν (cm^{-1})

3. The Crystal and Molecular Structure Determination of Tris(hexacarbonyldicobalt-π-ethynyl)arsine

A crystal with approximate dimensions 0.1x0.1x0.1 mm was mounted on a goniometer head and alignment photographs were recorded on the Weissenberg camera. The oscillation photographs obtained showed *mm* symmetry. A zero level Weissenberg photograph showed the monoclinic a^*c^* zone. The crystal was thus mounted along the unique axis b of the monoclinic cell. The first level Weissenberg showed that twice as many festoons appeared which cut the axis corresponding to c^* than were present on the zero level. This implied a c glide plane perpendicular to b, since the condition for systematic absences is, for all on $h0l$, $l = 2n + 1$.

The goniometer head was then transferred to the precession camera where the azimuthal angle was set to correspond to the a^* axis and alignment was effected on the $hk0$ zone. A systematic absence along b^* indicated a two-fold screw axis (for $0k0$, $k = 2n + 1$). The space group was thus assigned to be $P2_1/c$ (No. 14) and this was further confirmed by the $0kl$ precession zone which showed every second spot missing on the b^* axis (due to the two-fold screw axis) and the c^* axis (due to the c glide plane).

The difference between the two azimuthal settings for the precession zones determined the angle β^* as 67.6°. A measurement of the spacing on the precession zones gave a y_a distance of 3.99 mm, a y_b distance of 2.24 mm and a y_c distance of 2.71 mm. This corresponds to reciprocal dimensions of 0.093^{597} Å^{-1}, 0.0524^{85} Å^{-1} and 0.0635^{95} Å^{-1} respectively for a^*, b^* and c^*. Using the conversions for the monoclinic cell,[124] the film-measured direct cell dimensions are a = 11.56Å, b = 19.05Å, c = 17.01Å and β = 112.4°. The unit cell volume is thus 3452Å^3.

The density of the crystal was measured by flotation of crystals of the same crop in an iodoethane-benzene solution. The observed density was 1.88(2) g cm^{-3}. This was congruent with a calculated density of 1.94 g cm^{-3} based on four molecules of tris(hexacarbonyldicobalt-π-ethynyl)arsine, M = 1007.8 amu, in the monoclinic unit cell. The molecular volume was calculated to be 863Å^3.

The goniometer head was mounted on the diffractometer and both the (6,0,0) and the (0,0,6) reflections were centered. The (0,12,0) reflection was then located and centered. The twelve reflections used for the least squares refinement were (6,0,0), (-6,0,0), (0,12,0), (0,-12,0), (0,0,6), (0,0,-6), (4,4,4), (-4,-4,-4), (-4,4,8), (4,-4,-8), (4,-4,4), (-4,4,-4). The second least squares refinement cycle resulted in but small changes in the fourth decimal place of the cell parameters. The refined cell parameters are $a = 11.536 \pm 0.006$, $b = 19.031 \pm 0.011$, $c = 17.009 \pm 0.010$Å, $\beta = 112.30 \pm 0.03°$.

Data collection was initiated using the parameters listed in Table III-B-2. The quarter sphere collected was that bounded by positive k and positive l. Of the 4922 reflections collected, 3906 were accepted, 592 were less than 3σ and 424 were absent. A reject routine eliminating reflections with negative h on the $hk0$ zone as well as systematic absences in $P2_1/c$ was used. No absorption corrections were applied ($\mu = 40.10$ cm^{-1}) although they were most probably necessary. A simple calculation based on a two-dimensional model gave a minimum and a maximum transmission factor (I/I_o) of 0.67 and 0.76 respectively for the crystal used.

Normalized structure factors E_{hkl} were computed using the program *NORMA*. The value of ε was set to 1 for all reflections except those on the $h0l$ zone and on the $0k0$ axis for which it was set equal to 2. There were 2573 reflections processed with $(\sin^2\theta)/\lambda^2$ less than 0.21, 784 having E_{hkl} greater than 1.0, 113 having E_{hkl} greater than 2.0 and 10 reflections having E_{hkl} greater than 3.0.

A value of 1.90 was chosen for the minimum E value and the statistical phasing program *REL* was used to phase the data. The number of reflections with E_{hkl} greater

TABLE III-B-2

DATA COLLECTION PARAMETERS FOR TRIS(HEXACARBONYLDICOBALT-π-ETHYNYL)ARSINE

Radiation used:	Mo K_{α} (λ = 0.71069Å)
Pulse height analyzer	100%
Upper level	6.50
Lower level	2.50
Attenuators	Used
Space group routine used:	$P2_1/c$
maximum h: 11	minimum h: -12
maximum k: 20	minimum k: 0
maximum l: 17	minimum l: 0
maximum 2θ: 45.0°	minimum 2θ: 4.5°
Standard used *(hkl)*	(2,0,0)
Interval	every 30 reflections
Value and Variation	26000 ± 10%
Background	20 second counts
Base length of scan	2.5°
Total number of reflections collected:	4922

than 1.90 was 139. A sorting order was chosen such that the triples were signed in the order of their decreasing E_{hkl} magnitudes. Two options were used for the treatment of signs. In the first pass, *NBACK* was 1 and in the second pass, the *NBACK* $\neq$ 0 option was used. The maximum number of cycles was 20.

For space group $P2_1/c$, three seminvariants are necessary, all of which must not possess even-even-even parity. The second reflection must have parity different from the first and the third reflection must, along with having parity different from the first two, have parity different from the sum of the first two. The signs of these origin-determining reflections were all set to plus. The value of *PROBK* was 0.07. *PROB1* and *PROB2* were set to 0.93 and 0.70 respectively. The starting set involved the seven reflections listed in Table III-B-3 with their E_{hkl} values all signed according to the correct solution.

The consistency index *C* after the first pass for this solution was 0.98 and there were no additions or changes after 7 cycles. The second pass afforded a *C* of 0.98 in but two cycles. The second highest *C* was 0.88. In both passes, for the correct solution, the signs of the starting set were not predicted to be different from those originally assigned. There were 69 pluses and 70 minuses in the 139 reflections phased.

TABLE III-B-3

THE STARTING SET FOR THE SUCCESSFUL *REL'* SOLUTION OF TRIS(HEXACARBONYLDICOBALT-π-ETHYNYL)ARSINE

h	k	l	E_{hkl}
1	3	0	3.75
-4	3	8	3.72
0	14	1	3.16
-10	3	8	-3.43
-7	7	2	-3.28
-7	7	4	3.09
3	3	0	-3.06

An E-map was computed using the 139 reflections and their E_{hkl} from *REL*. One-quarter of the unit cell was computed (full x, $0 \rightarrow \frac{1}{2}$ in y and $0 \rightarrow \frac{1}{2}$ in z) with one-third angstrom resolution. From this map, five atoms were located and their approximate co-ordinates were recorded.

A structure factor calculation based on the positions of the arsenic atom and four cobalt atoms was carried out. The scale factor used here was 0.38. For 3906 reflections, the discrepancy index was 47%. An observed Fourier followed which yielded the positions of the remaining cobalt atoms and the acetylenic carbons. The main core of the molecule was now found.

Another structure factor calculation based on the positions of the arsenic atom, 6 cobalts and 6 acetylenic carbons gave an *R* factor of 38% for 3906 reflections. A difference Fourier synthesis now permitted location of most of the remaining atoms in the structure. The *RMAX* for this difference Fourier was 8.46. Only two carbonyls resisted positive identification but they were located after the first isotropic cycle of refinement by another difference Fourier synthesis.

The least squares refinement of tris(hexacarbonyl-dicobalt-π-ethynyl)arsine is summarized in Table III-B-4 which lists the parameters which best reflect the

TABLE III-B-4

STRUCTURE FACTOR INFORMATION FOR TRIS(HEXACARBONYLDICOBALT-π-ETHYNYL)ARSINE[a]

	BEFORE REFINE-MENT	ISO(1)	ISO(2)	ISO(3)	ANISO (1)c	ANISO (2)d	ANISO (3)	ANISO (4)
Scale Factor	0.3800	0.3515	0.3834	0.3859	0.3930	0.3989	0.3983	0.3983
Number of Matrices		2	2	2	2	5	5	
Total # of Parameters		197	197	262	262	442	442	
Number of Reflections	3906	3906	3134[b]	3214	3240	2691	2692	2692
"Goodness of fit"	9.216		3.787	3.328	2.361	1.595	1.487	1.487
R	37.6	25.2	18.9	17.1	14.2	9.3	8.4	8.4
R (with rejects out)	37.6	25.1	12.9	11.8	9.0	7.5	6.7	6.7
R_w	31.6	23.0	13.3	11.6	9.0	5.7	5.3	5.3
R_w (with rejects out)	31.6	22.9	11.6	10.2	7.3	5.0	4.7	4.7

a The structure factor calculation data listed is for that run immediately AFTER the least squares refinement cycle heading the column.

b A reject routine was introduced at this time.

c Only arsenic, six cobalts and the acetylenic carbons were ANISO.

d The original data was reprocessed using the method for calculation of *sigma* described in Chapter II, Section B. This accounts for the change in the number of reflections used. All atoms were ANISO.

effect of the refinement cycles. The isotropic refinement was started with all but four atoms located by observed and difference Fourier syntheses. The starting isotropic temperature factors were arbitrarily set at 2.0 for arsenic, 2.5 for cobalts, 4.0 for carbon atoms and 5.0 for oxygens. Two matrices were required and the atoms were not moved from one matrix to the other for the isotropic stage of refinement.

The addition of four atoms (four parameters each) brought the total number of parameters to 197 for isotropic least squares refinement. The drop in the number of reflections used after the second isotropic cycle is due to the introduction of a reject routine. This routine excluded all reflections where the difference between F_{obs} and F_{cal} was greater that 50% of F_{obs}. The weighted discrepancy factor R_w for all data dropped to 11.6% after isotropic refinement had converged. Anomalous dispersion corrections of $\Delta f' = 0.4$ and $\Delta f'' = 1.1$ for cobalt and $\Delta f' = 0.1$ and $\Delta f'' = 2.2$ for arsenic were applied to the mean atomic scattering factors at this time. Anisotropic refinement of the arsenic atom, the six carbons and six acetylenic carbons along with isotropic refinement of the rest of the atoms brought this discrepancy factor down another 2.6% in the first anisotropic cycle.

The positions and thermal parameters were allowed to refine anisotropically in 5 matrices. The moving of atoms from one matrix to another between anisotropic cycles assured a degree of correlation between them. The matrix location for each atom is listed in Appendix A (page 332).

Anisotropic convergence was attained by the fourth anisotropic cycle. In most cases, the shifts in the 442 refined parameters were smaller (by an average factor of 3) than their corresponding estimated standard deviations. A final structure factor calculation indicated that the weighted discrepancy factor for all the data was 5.3%.

A final difference Fourier synthesis with *RMAX* set to 8.46 showed no peaks higher that 0.9 $\Delta e\text{Å}^{-3}$. Considerable residual electron density about the refined cobalt atom positions made the assignment of hydrogen atom positions ambiguous and undesireable.

A list of observed and calculated structure factors can be found in Appendix A (page 332) of this Thesis. All reflections for which $(|F_{obs} - F_{cal}|/F_{obs})$ is greater than 0.5 are not listed. The final refined positional and thermal parameters for tris(hexacarbonyldicobalt-π-ethynyl)-arsine are also given in Appendix A.

SECTION C. RESULTS AND DISCUSSION

1. Non-crystallographic

Studies have been carried out on species which form π bonds with dicobaltoctacarbonyl and those which form σ bonds but, at the time this study was undertaken, no studies had been effected on ligands which possess both bonding possibilities. The aim of the research problem was to determine what type of bonding was likely to prevail in the reaction of triacetylenic arsines and phosphines with various transition metal carbonyls. The only successful result was obtained with triethynylarsine and dicobaltoctacarbonyl and the bonding preference is for the π type.

When three moles of $Co_2(CO)_8$ are added to one mole of triethynylarsine in an inert solvent, gas is immediately evolved with the formation of tris(hexacarbonyl-dicobalt-π-ethynyl)arsine. Even with one mole $Co_2(CO)_8$ and two moles of triethynylarsine the reaction still gave the same product (Appendix F). The reaction is described by Equation III-C-1. The lone pair apparently does not interact to displace terminal carbonyl ligands on the $Co_2(CO)_8$ molecule but rather, each of the three acetylenic linkages accommodates a $Co_2(CO)_6$ unit in π fashion just as with $Co_2(CO)_6$.

(PhCCPh).[77] Since this work has been reported[125] Carty *et al.*[120] have published a report on the X-ray crystal structure of $Co_4(CO)_{10}(Ph_2PCCCF_3)_2$ in which the ligand $Ph_2PC{\equiv}CCF_3$ was found both to σ bond (to a $Co_2(CO)_5$ unit) through the phosphorus atom and π bond *via* the C≡C moiety to another $Co_2(CO)_5$ unit forming a dimeric structure.

$$As(C{\equiv}CH)_3 + 3Co_2(CO)_8 \longrightarrow As(CCHCo_2(CO)_6)_3 + 6CO\uparrow \qquad \text{III C-1}$$

As can be seen from a quick survey of Appendix F, many reactions of triacetylenicarsines with transition metal carbonyls were tried with varying degrees of success. When $As(C{\equiv}CCH_3)_3$ and $As(C{\equiv}C\text{-}t\text{-}C_4H_9)_3$ were reacted with $Co_2(CO)_8$ more than one product was shown to exist by column chromatography and it is suspected σ bonded products probably exist. These products should be examined more thoroughly. Perhaps the donor ability of the arsenic atom is enhanced through the σ bonding system due to the presence of the alkyl groups. Again, perhaps the steric crowding observed in tris(hexacarbonyldicobalt-π-ethynyl)arsine is compounded by the presence of bulkier alkyl groups. This would have the effect of destabilizing the π bonded product in favour of the σ bonded product.

Complexes with other transition metal carbonyls were not as tractable and they were not examined very closely. Appendix F gives a list of the various reactions attempted, the reaction conditions and the product descriptions if any products were recovered. The iron carbonyls were the most systematically studied of the transition metal carbonyls. Chemical analyses were carried out on independently-prepared samples where great care was exercised to exclude air at all times. The fluffy light brown powder (insoluble in all common organic solvents) gave analytical results which differed by 5% in carbon, 2.5% in iron and 4% in arsenic. This led to the conclusion that the product was a polymer with rather variable stoichiometry.

The infrared spectrum of the ligand $As(C{\equiv}CH)_3$[121,123] shows a peak at 3291 cm^{-1} (C-H stretching vibration) which is moved to lower energy (3118 cm^{-1} and 2971 cm^{-1}) in tris-(hexacarbonyldicobalt-π-ethynyl)arsine. An even more dramatic change occurs to the peak at 2045 cm^{-1} (C≡C stretch) in the ligand which moves to 1438 cm^{-1} and 1418 cm^{-1} in the complex indicating the bond is more adequately described as double rather than triple upon complexation. These last bands were not visible on the infrared spectra run in KBr but they were observed in infrared spectra recorded using tetrachloroethylene solutions.

The infrared spectrum of dicobaltoctacarbonyl indicates terminal carbonyl stretching vibrations at 2068, 2041, 2024 cm^{-1} and a shoulder at 1992 cm^{-1}.[12] The bridging carbonyl band was recorded at 1860 cm^{-1} with a shoulder at 1825 cm^{-1}. When the bridging carbonyls are replaced by an acetylene, the bridging carbonyl frequencies disappear and the terminal carbonyls absorb at 2092, 2049 and 2024 cm^{-1}. In tris(hexacarbonyldicobalt-π-ethynyl)arsine, there are essentially three peaks recorded at 2090, 2068 and 2029 cm^{-1} and a shoulder at 2058 cm^{-1} on the 2068 cm^{-1} peak (see Figure III-B-1). The bonding of the $Co_2(CO)_6$ fragment to the acetylene can thus be suspected of being very similar to that in $Co_2(CO)_6(PhCCPh)$.[77]

The nuclear magnetic resonance (nmr) spectrum of the free ligand ($As(C{\equiv}CH)_3$) in dichloromethane solution shows a single sharp resonance at δ = 2.72 ppm which is normal for an unconjugated acetylenic proton.[127] When the $Co_2(CO)_6$ unit is complexed with the acetylenic linkage, the proton (in dichloromethane solution) is found to absorb at δ = 6.3 ppm. This is in the region of a proton attached to a double bonded carbon atom.

The complexed ligand retains the lone pair on the arsenic atom and this might be thought to afford a further bonding site. Attempts to react tris(hexacarbonyldicobalt-π-ethynyl)arsine with various Lewis acids were unsuccessful however and steric crowding as well as decreased donor ability of the arsine at the outset may well be responsible for this.

2. The Crystal and Molecular Structure of Tris(hexacarbonyldicobalt-π-ethynyl)arsine

Tris(hexacarbonyldicobalt-π-ethynyl)arsine crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. The molecules are discrete with a central triethynylarsine unit accommodating three $Co_2(CO)_6$ moieties which are each π bonded to one of the three acetylenic linkages. A picture of the molecular configuration is given in Figure III-C-1 where the heavy atoms are 'shaded' and the numbering scheme is given. It will be noted that three-fold symmetry is closely approximated in this view of the molecule down the *pseudo* three-fold axis. The $Co_2(CO)_6$ units are aligned such as to minimize carbonyl-arsenic contacts.

Tables III-C-1 and III-C-2 give the bond lengths and angles respectively for the complex. These parameters are arranged in such a way that the *pseudo* three-fold nature of the complex is shown. The average Co-Co bond length is 2.470(3)Å which further confirms the rather consistent value of this distance in these π bonded complexes: $Co_2(CO)_6 \cdot$ (PhCCPh) - 2.47Å,[77] $Co_3(CO)_9C_3HCo_2(CO)_6$ - 2.45Å,[110] $Co_6(CO)_{18}C_6Co_2(CO)_6$ - 2.47Å[111] and 2.46Å,[112] $Co_2(CO)_6 \cdot C_6F_6$ - 2.49Å.[115]

The angles subtended at the arsenic atom average

Figure III-C-1. The molecular configuration of tris(hexacarbonyldicobalt-π-ethynyl)arsine.

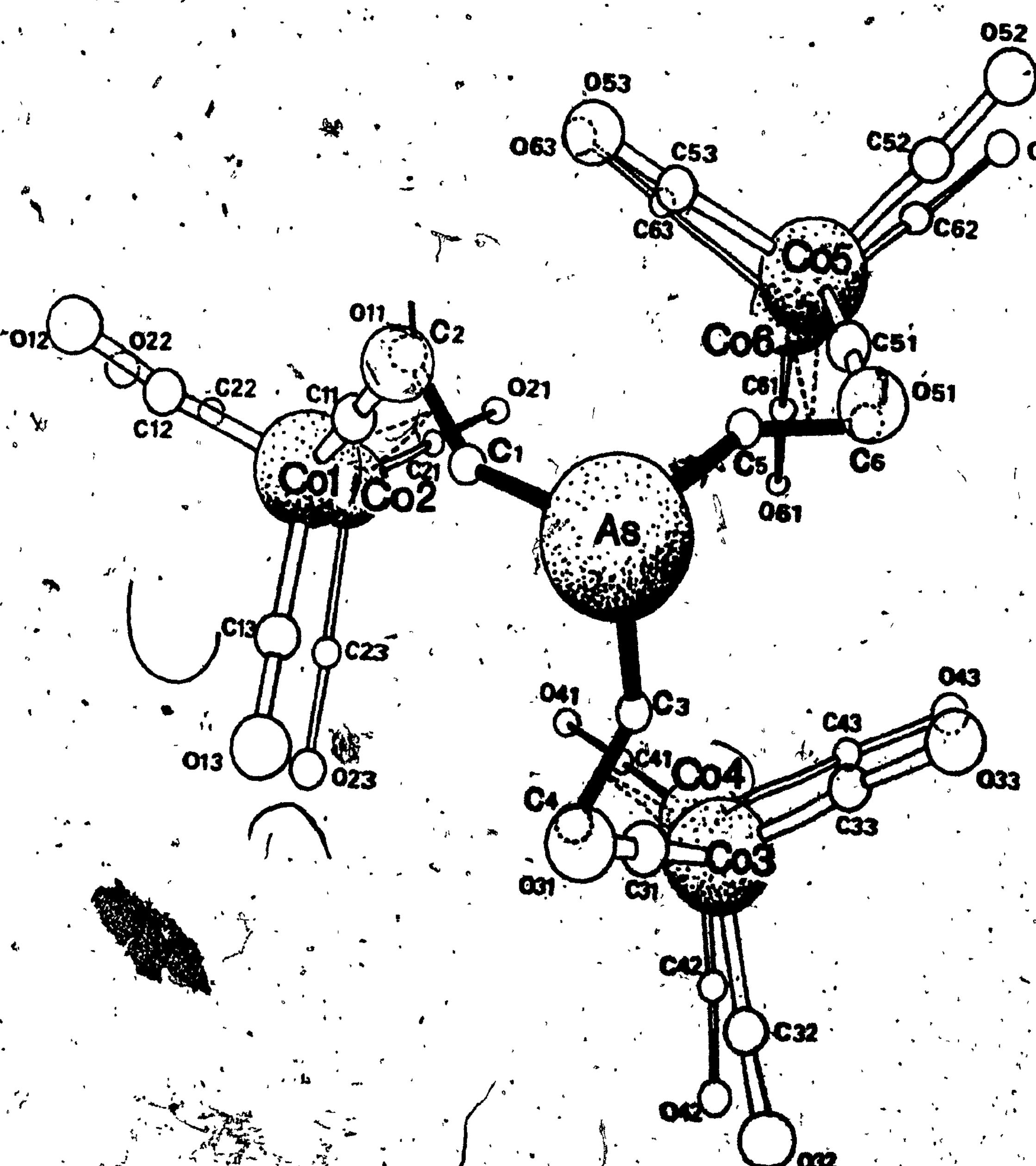

O52
O53
O63
C53
C52
O62
C63
C62
Co5
O11
C2
O12
O22
Co6
C51
O21
C61
O51
C22
C11
C12
C1
C5
C6
C21
Co1
Co2
O61
As
C13
C23
O41
C3
O43
C43
C41
O13
O23
Co4
O33
C4
C33
Co3
O31
C31
C42
C32
O42
O32

TABLE III-C-1

BOND LENGTHS (Å) IN TRIS(HEXACARBONYLDICOBALT-π-ETHYNYL)ARSINE

As –C1	1.954(12)	As –C3	1.960(10)	As –C5	1.943(12)
C1 –C2	1.352(18)	C3 –C4	1.316(17)	C5 –C6	1.326(17)
Co1–Co2	2.468(03)	Co3–Co4	2.477(03)	Co5–Co6	2.466(03)
Co1–C1	1.976(12)	Co3–C3	2.005(10)	Co5–C5	1.989(12)
Co1–C2	1.983(12)	Co3–C4	1.953(13)	Co5–C6	1.980(12)
Co2–C1	1.936(12)	Co4–C3	1.939(11)	Co6–C5	1.944(12)
Co2–C2	1.941(12)	Co4–C4	1.940(13)	Co6–C6	1.935(12)
Co1–C11	1.763(14)	Co3–C31	1.738(18)	Co5–C51	1.720(17)
Co1–C12	1.788(16)	Co3–C32	1.862(16)	Co5–C52	1.840(15)
Co1–C13	1.864(16)	Co3–C33	1.787(27)	Co5–C53	1.735(19)
Co2–C21	1.729(16)	Co4–C41	1.721(15)	Co6–C61	1.798(17)
Co2–C22	1.793(18)	Co4–C42	1.810(18)	Co6–C62	1.848(17)
Co2–C23	1.815(14)	Co4–C43	1.761(19)	Co6–C63	1.780(16)
C11–O11	1.170(19)	C31–O31	1.175(22)	C51–O51	1.202(22)
C12–O12	1.142(20)	C32–O32	1.088(19)	C52–O52	1.086(19)
C13–O13	1.099(18)	C33–O33	1.126(31)	C53–O53	1.148(24)
C21–O21	1.174(20)	C41–O41	1.164(18)	C61–O61	1.117(22)
C22–O22	1.165(23)	C42–O42	1.133(22)	C62–O62	1.135(21)
C23–O23	1.143(17)	C43–O43	1.186(22)	C63–O63	1.146(20)

TABLE III-C-2

BOND ANGLES (°) IN TRIS(HEXACARBONYLDICOBALT-π-ETHYNYL)ARSINE

C1 -As -C3 :	102.0(5)	C3 -As -C5 :	104.3(5)	C5 -As -C1 :	103.6(5)
As -C1 -C2 :	141.0(9)	As -C3 -C4 :	141.7(9)	As -C5 -C6 :	139.2(9)
As -C1 -Co1:	119.0(6)	As -C3 -Co3:	119.6(6)	As -C5 -Co5:	119.7(6)
As -C1 -Co2:	146.6(7)	As -C3 -Co4:	146.0(6)	As -C5 -Co6:	148.3(7)
Co1-C1 -C2 :	70.3(7)	Co3-C3 -C4 :	68.5(7)	Co5-C5 -C6 :	70.1(7)
Co2-C1 -C2 :	69.8(7)	Co4-C3 -C4 :	70.2(7)	Co6-C5 -C6 :	69.6(7)
Co1-C1 -Co2:	78.2(4)	Co3-C3 -Co4:	77.8(4)	Co5-C5 -Co6:	77.7(4)
Co1-C2 -C1 :	69.8(7)	Co3-C4 -C3 :	72.7(8)	Co5-C6 -C5 :	70.8(7)
Co2-C2 -C1 :	69.4(7)	Co4-C4 -C3 :	70.2(8)	Co6-C6 -C5 :	70.4(7)
Co1-C2 -Co2:	77.9(4)	Co3-C4 -Co4:	79.0(5)	Co5-C6 -Co6:	78.1(4)
C1 -Co1-C2 :	39.9(5)	C3 -Co3-C4 :	38.8(5)	C5 -Co5-C6 :	39.0(5)
C1 -Co1-Co2:	50.2(3)	C3 -Co3-Co4:	49.9(3)	C5 -Co5-Co6:	50.3(3)

TABLE III-C-2 (CONT'D)

C1 -Co1-C13:	101.4(6)	C3 -Co3-C33:	104.6(8)	C5 -Co5-C53:	104.6(7)
C1 -Co1-C11:	100.9(6)	C3 -Co3-C31:	99.1(6)	C5 -Co5-C51:	100.7(7)
C11-Co1-C2 :	96.3(6)	C31-Co3-C4 :	98.8(7)	C51-Co5-C6 :	95.5(7)
C2 -Co1-Co2:	50.3(4)	C4 -Co3-Co4:	50.2(4)	C6 -Co5-Co6:	50.1(3)
Co2-Co1-C13:	103.2(5)	Co4-Co3-C33:	99.1(9)	Co6-Co5-C53:	103.1(8)
C13-Co1-C11:	100.3(6)	C33-Co3-C31:	101.2(9)	C53-Co5-C51:	103.2(9)
C11-Co1-C12:	98.0(7)	C31-Co3-C32:	97.7(8)	C51-Co5-C52:	96.6(8)
C13-Co1-C12:	106.8(7)	C33-Co3-C32:	109.0(9)	C53-Co5-C52:	103.2(7)
C2 -Co1-C12:	106.0(6)	C4 -Co3-C32:	101.0(6)	C6 -Co5-C52:	106.8(6)
Co2-Co1-C12:	98.6(5)	Co4-Co3-C32:	100.4(5)	Co6-Co5-C52:	99.2(6)
Co2-Co1-C11:	145.8(5)	Co4-Co3-C31:	146.6(6)	Co6-Co5-C51:	145.1(6)
C1 -Co2-C2 :	40.8(5)	C3 -Co4-C4 :	39.7(5)	C5 -Co6-C6 :	40.0(5)
C1 -Co2-Co1:	51.6(3)	C3 -Co4-Co3:	52.3(3)	C5 -Co6-Co5:	52.0(4)
C1 -Co2-C23:	106.5(6)	C3 -Co4-C43:	106.6(7)	C5 -Co6-C63:	106.7(6)
C1 -Co2-C21:	102.4(7)	C3 -Co4-C41:	101.4(6)	C5 -Co6-C61:	101.9(6)
C21-Co2-C2 :	101.0(6)	C41-Co4-C4 :	100.8(6)	C61-Co6-C6 :	100.8(6)
C2 -Co2-Co1:	51.8(4)	C4 -Co4-Co3:	50.7(4)	C6 -Co6-Co5:	51.8(4)
Co1-Co2-C23:	97.8(6)	Co3-Co4-C43:	100.6(6)	Co5-Co6-C63:	99.1(5)

TABLE III-C-2 (CONT'D)

C23-Co2-C21:	102.6(7)	C43-Co4-C41:	100.6(8)	C63-Co6-C61:	101.1(8)
C21-Co2-C22:	96.9(8)	C41-Co4-C42:	95.7(7)	C61-Co6-C62:	96.4(7)
C23-Co2-C22:	103.4(7)	C43-Co4-C42:	104.9(7)	C63-Co6-C62:	102.9(7)
C2 -Co2-C22:	100.9(7)	C4 -Co4-C42:	102.3(6)	C6 -Co6-C62:	103.1(6)
Co1-Co2-C22:	98.0(6)	Co3-Co4-C42:	98.8(6)	Co5-Co6-C62:	99.1(5)
Co1-Co2-C21:	151.1(6)	Co3-Co4-C41:	150.3(5)	Co5-Co6-C61:	151.0(6)
Co1-C11-O11:	177.2(13)	Co1-C12-O12:	178.2(15)	Co1-C13-O13:	179.6(14)
Co2-C21-O21:	178.5(15)	Co2-C22-O22:	178.0(17)	Co2-C23-O23:	176.8(14)
Co3-C31-O31:	175.9(18)	Co3-C32-O32:	177.8(15)	Co3-C33-O33:	175.3(25)
Co4-C41-O41:	178.9(13)	Co4-C42-O42:	177.5(14)	Co4-C43-O43:	175.5(17)
Co5-C51-O51:	172.5(16)	Co5-C52-O52:	178.1(14)	Co5-C53-O53:	175.6(16)
Co6-C61-O61:	177.3(16)	Co6-C62-O62:	176.0(14)	Co6-C63-O63:	177.0(15)

103.3° which is in agreement with angles (average 101°) found in other arsines.[128-130] Although the X-ray crystallographic structure of triethynylarsine has not been reported, that of triethynylphosphine [131] shows angles which average 101°. The slight increase in C-As-C angle can doubtless be attributed to the fact that the substituents are more bulky and cause a spreading of the three units away from each other.

In the molecule triethynylphosphine, there exists an angle at the carbon atoms adjacent to the phosphorus atom different from 180°. There appears to be a bending upwards (170° average) of the acetylenic moiety toward the phosphorus atom. A projection down the *pseudo* three-fold axis shows no bend in the other directions. The authors do not attempt an explanation of this phenomenon but it may result from a favoured contribution of one of the two mutually perpendicular π molecular orbitals to P-C bonding. The length of the phosphorus-carbon bond should be examined in this context.

The measured value of the average P-C(sp) bond is 1.75Å as reported by Kroon *et al.*[131] The difference between the radii of sp^2 and sp hybridized carbon atoms is 0.07Å.[132]

An average value of 1.86Å is obtained from values quoted for various P-C(sp^2) distances in diphosphine complexes[133-136]. Since the measured P-C distance in triethynylphosphine is 1.75Å, there appears to be some double bond character to the bond. It is likely that the same effect would be observed in the arsenic analog.

In tris(hexacarbonyldicobalt-π-ethynyl)arsine, the As-C distance averages 1.952(5)Å. An average As-C distance of 1.97Å is found from examination of various diarsine complexes.[137-140] Since these values are approached in tris(hexacarbonyldicobalt-π-ethynyl)arsine, it is assumed that, upon complexation the degree of participation of the acetylenic π orbitals in the As-C bond is reduced. The π orbitals are assumed to be mostly involved in bonding to the $Co_2(CO)_6$ fragment.

The angles at the acetylenic carbon atoms attached to phosphorus in triethynylphosphine average 170°[131] whereas the angles at C1, C3 and C5 in tris(hexacarbonyldicobalt-π-ethynyl)arsine average 140.6°. This implies more p character to this carbon atom which approaches sp^2 hybridization. The average C-C bond length of 1.331(11)Å supports this claim (double bond radius of carbon is 0.667Å[132]) and it is similar to other values which have been reported for this type of complex: $Co_2(CO)_6(PhCCPh)$ - 1.37Å,[77] $Co_3(CO)_9C_3HCo_2(CO)_6$ - 1.34Å,[110] $Co_6(CO)_{18}C_6 \cdot Co_2(CO)_6$ - 1.37Å[111] and 1.37Å,[112] $Co_2(CO)_6C_6F_6$ - 1.36Å.[115]

The position of the hydrogen atoms in this compound are of certain interest but they could not satisfactorily be found by final difference synthesis. The average angle formed between the As-C-C planes and the planes perpendicular to the Co-Co bond is 25.2° and the position of the hydrogen atom attached to the adjacent carbon in relation to this is of significance. It is expected that the C-H bond vector would form a similar angle with the plane perpendicular to the Co-Co bond but in the opposite direction.

The cobalt-acetylenic carbon bonding scheme will now be discussed in detail. As with all other similar compounds, the angle between the cobalt-cobalt vector and the acetylenic carbon-carbon vector is very close to 90° (Co1-Co2/C1-C2: 89.9°, Co3-Co4/C3-C4: 91.8°, Co5-Co6/C5-C6: 90.0°). The novel feature in this bonding however is the fact that the plane of the two acetylenic carbon atoms and the arsenic atom is not perpendicular to the cobalt-cobalt bond. The arsenic atom thus plays a role in repelling one of the two $Co_2(CO)_6$ cobalt atoms and its substituents. Table III-C-3 lists the non-bonded intramolecular contacts to 3.5Å. The arsenic-cobalt distances are listed. The

TABLE III-C-3

NON-BONDED INTRAMOLECULAR CONTACTS (Å) FOR TRIS(HEXACARBONYL-DICOBALT-π-ETHYNYL)ARSINE

As -Co1:	3.387	As -Co3:	3.426	As -Co5:	3.400
Co1-C22:	3.24	Co3-C42:	3.28	Co5-C62:	3.31
Co1-C23:	3.26	Co3-C43:	3.29	Co5-C63:	3.26
Co2-C12:	3.26	Co4-C32:	3.36	Co6-C52:	3.30
Co2-C13:	3.42	Co4-C33:	3.28	Co6-C53:	3.32
C1 -C3 :	3.04	C3 -C5 :	3.08	C1 -C5 :	3.06
C1 -C11:	2.89	C3 -C31:	2.85	C5 -C51:	2.86
C1 -C13:	2.97	C3 -C33:	3.00	C5 -C53:	2.95
C1 -C21:	2.86	C3 -C41:	2.84	C5 -C61:	2.91
C1 -C23:	3.01	C3 -C43:	2.97	C5 -C63:	2.99
C2 -C11:	2.79	C4 -C31:	2.81	C6 -C51:	2.74
C2 -C12:	3.01	C4 -C32:	2.94	C6 -C52:	3.07
C2 -C21:	2.84	C4 -C41:	2.82	C6 -C61:	2.88
C2 -C22:	2.88	C4 -C42:	2.92	C6 -C62:	2.96
C4 -C23:	3.49	C4 -O23:	3.31	C6 -O43:	3.38
C11-C12:	2.68	C31-C32:	2.71	C51-C52:	2.66
C12-C13:	2.93	C32-C33:	2.97	C52-C53:	2.80
C11-C13	2.78	C31-C33:	2.72	C51-C53:	2.71
C21-C22:	2.64	C41-C42:	2.62	C61-C62:	2.72
C22-C23:	2.83	C42-C43:	2.83	C62-C63:	2.84
C21-C23:	2.77	C41-C43:	2.68	C61-C63:	2.76

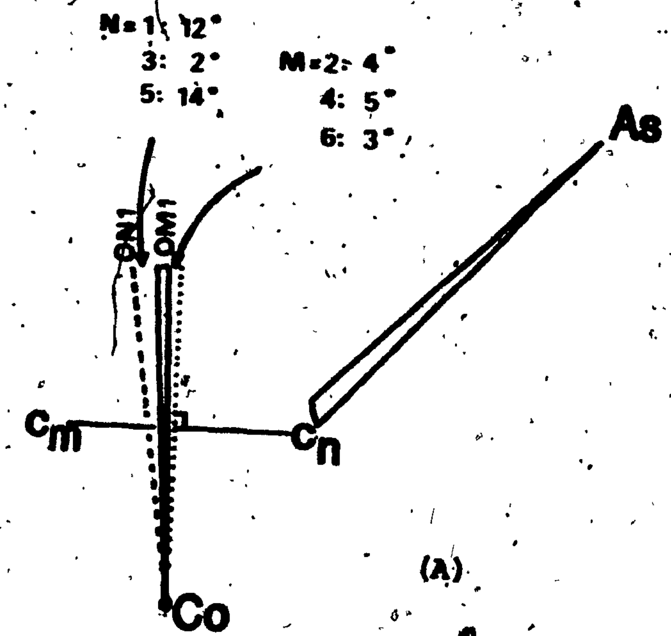
TABLE III-C-3 (CONT'D)

C12-C22:	2.99	C32-C42:	3.09	C52-C62:	3.06
C12-O22:	3.40	C32-O42:	3.46	C52-O62:	3.39
O12-C22:	3.38	O32-C42:	3.49	O52-C62:	3.41
O12-O22:	3.40	O32-O42:	3.49	O52-O62:	3.39
C13-C23:	3.16	C33-C43:	3.08	C53-C63:	3.15
C13-O23:	3.45	C33-O43:	3.42	C53-O63:	3.49
C21-O41:	3.30	C41-O61:	3.30	C61-O21:	3.37
O21-O41:	3.19	O41-O61:	3.22	O21-O61:	3.33
C23-O41:	3.45	C43-O61:	3.39	O43-O61:	3.46

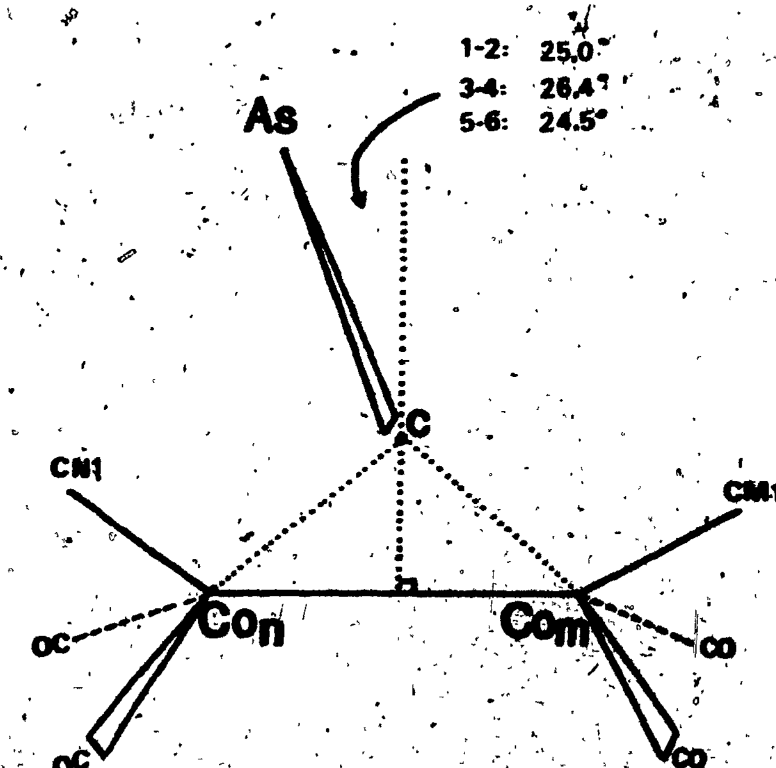
major contacts are observed between carbonyl carbon atoms on the same cobalt atom. Close contacts also exist between these carbonyl carbon atoms and the corresponding acetylenic carbon atoms. Other contacts are significant indicating that the molecule is under considerable steric strain. It is interesting that in spite of all the distortions, the orthogonality of the C–C/Co–Co bonds remains intact. This suggests that this feature is the most inviolable of them all. Figure III-C-2 shows two schematic representations of the molecule, (a) viewed down the Co–Co bond and (b) viewed down the acetylenic bond.

There is a steric interaction between the arsenic atom and the $Co_2(CO)_6$ moiety which results in a twist of the carbonyls about the Co–Co bond. This twist is 4° and 3° for the more remote carbonyl (C*m*1 where $m = 2$ and 6 respectively) and 12° and 14° in the case of the closest carbonyl (C*n*1 where $n = 1$ and 5 respectively). There is also a smaller twist in the same direction of the carbonyls on cobalts 3 and 4 although here the more remote carbonyl (C41) is twisted 5° away from the arsenic whereas C31 is only twisted by 2°. Another steric interaction occurs perpendicular to this one and is evidenced by the lengthening of the average acetylenic carbon–Co*n* ($n = 1,3,5$) bond (1.981(7)Å) in relation to the average acetylenic carbon-Co*m* ($m = 2,4,6$) bond (1.939(1)Å). The carbonyl adjacent to the arsenic atom (C*n*1) is pushed away from it which results in the bond length

Figure III-C-2. Two schematic representations of tris(hexacarbonyldicobalt-π-ethynyl)arsine, a) viewed down the Co-Co bond and b) viewed down the acetylenic bond.


N=1: 12°
3: 2°
5: 14°
M=2: 4°
4: 5°
6: 3°
As
ON1
OM1
Cm
Cn
Co

(A)


1-2: 25.0°
3-4: 26.4°
5-6: 24.5°
As
C
CN1
CM1
Con
Com
OC
OC
CO
CO

(B)

differences observed and in the Co*m*-Co*n*C*n*1 angle of 150.8° which is significantly greater than the Co*n*-Co*m*-C*m*1 angle of 145.8°. These angles straddle the value observed for $Co_5(CO)_{15}C_3H$ (147.9°).[110]

Interesting trends are observed in the carbonyl groups themselves which appear to be under the influence of the ligands which are *trans* to themselves in the albeit highly-distorted octahedral co-ordination about the cobalt atoms. The carbonyls which are *trans* to a cobalt atom display the shortest cobalt-carbon bond (average of six - 1.745(12)Å). Of the other two carbonyl types, the carbonyls which are *trans* to the acetylenic carbons bonded to the arsenic atom are longer (average of six - 1.824(12)Å) than those *trans* to the other acetylenic carbon (average of six - 1.790(18)Å). Inspection of Table III-C-1 will show that the individual values confirm the trends observed in these averages in most cases. The carbon-oxygen bond lengths average 1.144(8)Å and the average angle of bend at the carbonyl carbon is 177.0(4)°. Both these values are normal.

Table III-C-4 describes the thermal ellipsoids of vibration of the individual atoms in tris(hexacarbonyl-dicobalt-π-ethynyl)arsine. It will be noted that the vibrations are generally high and considerably anisotropic. This is not altogether surprising considering the rather free environment of the carbonyl groups on the cobalt fragments

TABLE III-C-4

THERMAL VIBRATION ELLIPSOIDS[a] - TRIS(HEXACARBONYLDICOBALT-π-ETHYNYL)ARSINE

Atom	Axes[b]	Direction Cosines		
As	3.88	0.36499	0.90002	0.23798
	3.24	0.23411	-.33620	0.91221
	2.21	0.90107	-.27737	-.33352
Co1	6.05	-.09650	0.56281	0.82094
	3.79	0.47886	-.69677	0.53393
	2.18	0.87259	0.44469	-.20241
Co2	4.95	-.36611	-.06514	0.92829
	4.21	0.23679	-.97127	0.02517
	3.14	0.89995	0.22888	0.37100
Co3	7.72	-.19996	-.47323	0.85796
	4.75	-.01009	0.87657	0.48117
	2.38	0.97979	-.08764	0.17991
Co4	6.97	0.27865	0.10800	0.95429
	3.29	0.03217	-.99415	0.10306
	2.29	0.95984	0.00214	-.28053
Co5	6.52	0.41636	0.12340	0.90078
	4.54	0.52281	0.77818	-.34821
	2.57	0.74404	-.61580	-.25952
Co6	5.12	-.05027	0.35209	0.93462
	3.34	0.59887	0.76097	-.25461
	3.06	0.80096	-.54494	0.24831
C1	5.96	0.50798	0.84699	0.15718
	3.26	0.72678	-.32324	-.60613
	1.95	0.46251	-.42204	0.77968
C2	5.27	0.44061	-.89770	0.01129
	4.33	0.50131	0.23548	-.83263
	2.54	0.74473	0.37240	0.55371
C3	4.71	0.27502	-.95525	0.10934
	2.60	0.25476	0.18202	0.94971
	1.39	0.92715	0.23318	-.29342
C4	8.77	0.21604	0.97581	-.03454
	3.95	-.10329	0.05800	0.99296
	0.40	0.97098	-.21079	0.11330
C5	5.31	0.16920	-.82144	0.54457
	3.15	0.42107	0.55987	0.71355
	0.98	0.89105	-.10852	-.44078

TABLE III-C-4 (CONT'D)

C6	5.13	0.89346	0.29503	0.33878
	2.96	-.04072	-.69800	0.71494
	1.89	0.44751	-.65250	-.61162
C11	11.97	0.47880	-.70483	-.52353
	3.74	0.74938	0.63876	-.17488
	1.24	0.45762	-.30855	0.83387
O11	13.92	0.17968	0.96998	0.16371
	9.99	0.94193	-.21780	0.25574
	3.96	-.28374	-.10820	0.95278
C12	7.98	0.07356	0.44656	0.89172
	7.20	0.53239	0.73855	-.41381
	4.63	0.84346	-.50510	0.18330
O12	20.53	0.48327	-.62576	-.61235
	12.53	0.45129	-.42127	0.78664
	2.70	0.75033	0.65647	-.07890
C13	7.45	-.08038	0.67459	0.73382
	6.37	0.95669	-.15460	0.24677
	1.82	0.28004	0.72182	-.63295
O13	11.99	-.01839	0.49129	0.87080
	6.70	0.46910	0.77342	-.42649
	2.89	0.88309	-.40057	0.24456
C21	12.89	0.09713	-.92582	0.36524
	4.71	0.99118	0.12341	0.04881
	2.84	-.09033	0.35726	0.92963
O21	12.61	0.30876	0.92027	0.24015
	8.34	0.95113	-.30017	-.07313
	5.08	-.00483	-.25100	0.96798
C22	12.99	0.51259	0.59182	-.62217
	6.85	-.12949	0.76950	0.62541
	6.15	0.84885	-.24003	0.47092
O22	18.11	0.63792	-.17453	-.75009
	13.69	0.27639	-.85711	0.43461
	5.18	0.71868	0.48466	0.49848
C23	8.79	0.74264	-.17105	-.64751
	5.42	0.66967	0.18298	0.71973
	1.98	-.00479	-.96812	0.25044
O23	11.21	0.53913	0.43462	-.72147
	7.13	0.46837	0.55716	0.68565
	3.51	0.70009	-.70759	0.09674

TABLE III-C-4 (CONT'D)

C31	16.94	0.38438	0.88541	-.26155
	4.25	0.52112	-.44184	-.73027
	2.08	0.76212	-.14432	0.63111
O31	20.74	0.23641	0.97050	0.04806
	7.00	0.96341	-.22748	-.14199
	4.94	0.12686	-.07984	0.98870
C32	11.52	-.27539	0.34004	0.89920
	6.96	-.03087	-.93799	0.34531
	4.27	0.96087	0.06746	0.26870
O32	15.43	-.13965	0.08559	0.98650
	11.83	0.18330	0.98130	-.05922
	0.99	0.97315	-.17239	0.15270
C33	24.80	-.15417	-.78087	0.60541
	11.83	0.31519	-.61955	-.71894
	2.41	0.93649	0.08001	0.34148
O33	25.73	0.41891	0.34250	-.84099
	14.58	0.86167	-.44235	0.24896
	5.88	0.28660	0.82886	0.48038
C41	7.02	0.50211	0.69401	0.51587
	4.53	0.70654	-.67334	0.21811
	2.22	0.49877	0.25489	-.82843
O41	9.37	0.21067	-.95252	0.21967
	7.89	0.86733	0.28592	0.40732
	4.32	0.45081	-.10466	-.88647
C42	11.26	0.54005	0.20419	0.81647
	4.94	0.81331	-.37636	-.44383
	2.91	0.21681	0.90369	-.36932
O42	17.40	0.36121	0.32158	0.87526
	6.90	0.02835	-.94202	0.33434
	3.18	0.93204	-.09583	-.34949
C43	12.40	0.27394	-.26938	0.92324
	7.73	0.48613	0.86717	0.10879
	1.95	0.82998	-.41887	-.36851
O43	18.16	0.40867	0.01973	0.91247
	5.94	0.87860	-.27934	-.38745
	3.48	0.24740	0.95999	-.13150
C51	14.35	0.00139	0.54334	0.24848
	7.81	-.04998	-.75350	0.93410
	2.85	0.59550	-.76145	-.25635

TABLE III-C-4 (CONT'D)

O51	18.64	0.74387	0.65271	-.14417
	10.91	0.60796	-.73479	0.18866
	6.34	0.02845	0.18454	0.98241
C52	10.69	0.27267	0.01654	0.96196
	4.29	0.36680	0.92262	-.11979
	2.56	0.88957	-.38536	-.24551
O52	18.76	0.36743	0.00827	0.93001
	8.53	0.87019	0.35619	-.34060
	2.18	0.32861	-.93438	-.13807
C53	18.71	0.60366	0.09018	0.79212
	9.55	0.76953	0.19390	-.60851
	0.05	0.20864	-.97687	-.04766
O53	30.85	0.39148	-.07579	0.91705
	8.74	0.74774	-.55479	-.36502
	3.82	0.53658	0.82853	-.16053
C61	9.94	0.84157	-.00804	-.54009
	5.31	0.24808	0.89380	0.37349
	3.35	0.47965	-.44839	0.75420
O61	16.61	0.58401	0.72999	0.35482
	7.31	0.61982	-.68344	0.38547
	4.85	0.52389	-.00520	-.85177
C62	8.26	-.17064	-.88724	0.42864
	6.95	0.41499	-.45921	-.78548
	2.93	0.89374	0.04393	0.44642
O62	14.73	-.28653	0.26940	0.91943
	9.51	0.94430	0.24185	0.22336
	3.72	0.16203	-.93216	0.32367
C63	8.86	0.83417	0.53623	-.12949
	6.73	0.05767	0.14864	0.97821
	3.64	0.54876	-.83088	0.09304
O63	17.34	0.57725	-.60677	-.63573
	7.13	0.10197	-.68023	0.72586
	4.09	0.87294	0.41124	0.26263

[a] Given in the order of major, median and minor axes.

[b] Axes lengths are in units of B where the root mean square displacement $(\bar{U}^2)^{\frac{1}{2}} = (B/8\pi^2)^{\frac{1}{2}}$.

for example. Table III-C-5 gives a list of intermolecular contacts to 3.5Å. It can be seen that the molecules are quite independent, no contacts being observed less than 3.0Å.

Finally, Figure III-C-3 shows a view of the packing of the four molecules in the unit cell. This is a view down the *a* axis of the monoclinic. From this view, the tilt of the $Co_2(CO)_6$ units away from the arsenic atom is clearly visible as well as the geometry of the cobalt carbonyl fragment.

TABLE III-C-5

INTERMOLECULAR CONTACTS (Å) FOR TRIS(HEXACARBONYLDICOBALT-π-ETHYNYL)ARSINE [a,b]

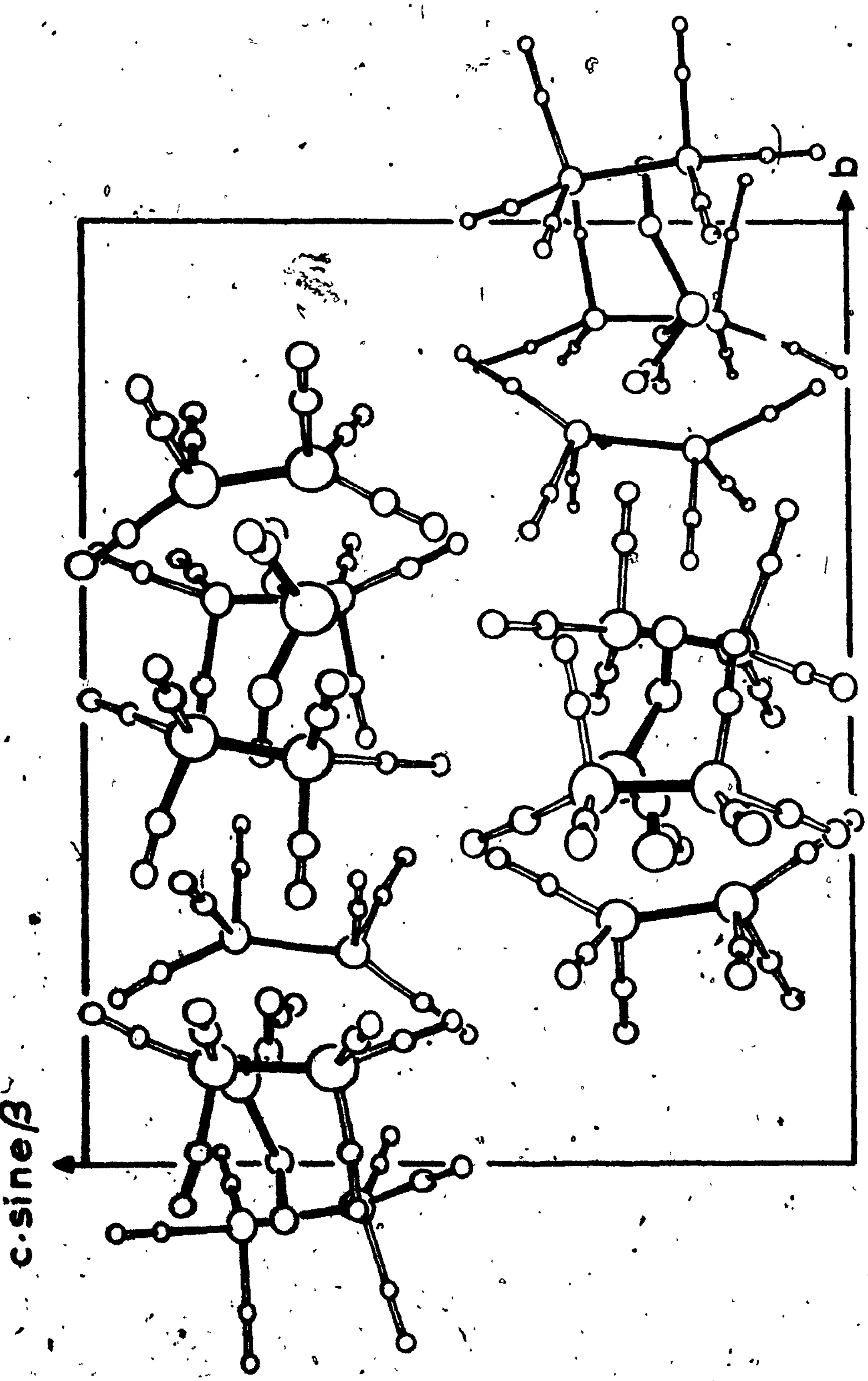
C6 -O23:	3.43 VI	O32-O53:	3.23 I	C52-O12:	3.43 V
O11-C23:	3.09 VIII	O41-O43:	3.36 III	O52-O12:	3.38 V
O11-O23:	3.07 VIII	C42-O61:	3.46 III	O52-C32:	3.47 VI
O11-O51:	3.40 IV	O42-O63:	3.12 I	O52-O32:	3.37 VI
O12-O21:	3.36 VIII	O43-C13:	3.27 VI	O52-C42:	3.14 VI
C13-O41:	3.30 VIII	O43-O13:	3.16 VI	O52-O42:	3.06 VI
O13-O41:	3.31 VIII	C43-O61:	3.27 III	O61-C42:	3.46 III
O21-C62:	3.46 II	O43-O41:	3.36 III	O61-C43:	3.27 III
O21-O62:	3.36 II	O43-O61:	3.31 III	O61-O43:	3.31 III
C31-O22:	3.40 VII	O51-O11:	3.40 IV	C61-O63:	3.33 II
O31-O22:	3.05 VII	C51-O23:	3.39 VI	O61-O63:	3.34 II
O31-C51:	3.16 IV	O51-O23:	3.36 VI	O62-O13:	3.47 VI
O31-O51:	3.18 IV	C51-O31:	3.16 IV	C62-O21:	3.46 II
O32-C11:	3.20 I	O51-O31:	3.18 IV	O62-O21:	3.36 II
O32-O11:	3.14 I	O51-O51:	3.08 IV	O63-C61:	3.33 II
C32-O53:	3.45 I	O52-C4 :	3.39 VI	O63-O61:	3.34 II

[a] Only atomic contacts less than 3.5Å are quoted.

[b] The following transformations give the position of the second atom listed relative to the first which has the co-ordinates (x, y, z) listed in Table A-2, Appendix A:

I	$1 + x, y, z$	V	$-x, \frac{1}{2} + y, \frac{1}{2} - z$
II	$-x, 1 - y, -z$	VI	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
III	$1 - x, 1 - y, -z$	VII	$1 + x, \frac{1}{2} - y, \frac{1}{2} + z$
IV	$-x, 1 - y, 1 - z$	VIII	$x, \frac{1}{2} - y, \frac{1}{2} + z$

Figure III-C-3. A projection down the *a* axis of the monoclinic cell showing the four molecules of tris(hexacarbonyldicobalt-π-ethynyl)-arsine.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CHAPTER IV. THE CRYSTAL AND MOLECULAR STRUCTURE OF μ-{BIS(DIPHENYLPHOSPHINO)METHANE}-μ-(DIPHENYLACETYLENE)TETRACARBONYLDICOBALT AND THE DI-μ-{BIS(DIPHENYLARSINO)METHANE}-μ-(DIPHENYLACETYLENE)DICARBONYLDICOBALT 1,2-DICHLOROETHANE SOLVATE COMPLEX.

SECTION A. INTRODUCTION

1. General Considerations

In Chapter III, the bonding of tertiary group VB ligands to transition metal carbonyls was discussed somewhat superficially. In this chapter, potentially bidentate ligands of phosphorus and arsenic will be reviewed from a structural point of view. It is interesting to compare the 'bites' of the various ligands (phosphorus-phosphorus or arsenic-arsenic distances) and correlate these with the various bonding modes exhibited by the complexes thev form. Two reviews have recently been published in this field.[141,142] There exists also a review [143] on the steric effects in bis-chelate complexes of molybdenum and tungsten.

Potentially most organic ligands containing more than one phosphorus and/or arsenic atom are bidentate.

This is not the case in complexes with ligands of the general form R_2P-PR_2 because the small 'bite' (P-P distance of $\sim$2.24 Å) which renders sigma bonding of both phosphorus atoms to the same metal atom impossible. These ligands are usually found to be bridging two transition metal carbonyl units as in the complexes $(CO)_5Mo((C_2H_5)_2P-P(C_2H_5)_2)Mo(CO)_5$,[144] $(CO)_4Fe((CH_3)_2P-P(CH_3)_2)Fe(CO)_4$[145] and $(CO)_3Ni((C_6H_5)_2P-P(C_6H_5)_2)Ni(CO)_3$[146] which have all been studied by X-ray crystallographic structure determination. Carty *et al.*[120] have studied the reaction of $Co_2(CO)_8$ with $(C_6H_5)_2P-C{\equiv}C-P(C_6H_5)_2$ and have found that the unsaturated linkage does not π bond to the cobalt carbonyl. Instead, the linear $P-C{\equiv}C-P$ skeleton joins two $Co_2(CO)_7$ units in the product $Co_2(CO)_7((C_6H_5)_2P-C{\cdot}C-P(C_6H_5)_2)Co_2(CO)_7$. These units retain the two bridging carbonyls of the presursor $Co_2(CO)_8$.

2. Complexes Containing $R_2MCH_2CH_2MR_2$

The most common complexes to have been studied by X-ray crystallography are those containing ligands of the form $R_2MCH_2CH_2MR_2$ where M = As, P. The geometry of the ligand is such that it is ideally suited to act as a bidentate chelating ligand. Many complexes of this type are known. This ligand has also been shown to bridge two substituted transition metal units. The complex $(CuCl((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)((C_6H_5)_2PCH_2))_2 \cdot 2C_3H_6O$ contains a diphenylphosphinoethane bridge, the carbon-carbon bond of which contains a center of inversion which relates the two halves of the molecule.[147] Another related copper complex, $\{Cu(N_3)((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)(C_6H_5)_2PCH_2\cdot\}_2$ [133] exhibits the same bonding pattern (the center of inversion is absent however). In both complexes, the copper atoms are tetrahedrally co-ordinated, two of the co-ordination sites being occupied by the ligand acting as a bidentate chelate.

Molybdenum forms complexes with 1,2-bis-(diphenylphosphino)ethane. Drew [148] reported the structure determination of a seven co-ordinate capped octahedral structure $MoBr_2(CO)_3((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)$ in which the bidentate ligand spans approximately octahedral sites. In another complex, $MoOCl((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)(ZnCl_3 \cdot CH_3COCH_3)$,[149] the two bidentate chelates are *trans* to one another in a roughly octahedral geometry. The oxygen and chlorine atoms are consequently also *trans*.

Rhenium forms a complex in which the two bidentate ligands $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ are *cis* to each other. In this complex $(ReH_3((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2)$,[150] the P-Re-P angles average 82.5°. The complex $ReH_3((C_6H_5)_2P\cdot CH_2CH_2P(C_6H_5)_2)(P(C_6H_5)_3)_2$ is also known.[151] Tully and Ginsberg [152] have reported infrared and nmr studies of the complex *trans*-$ReI(N_2)((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2$.

Several complexes of ruthenium with $R_2PCH_2CH_2PR_2$ have been studied by X-ray crystallography. The *trans*- isomer of $RuCl_2((C_6H_5)CH_3PCH_2CH_2PCH_3(C_6H_5))_2$ [153] as well as the ionic $Ru(NO)((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2^+$ [154] have been reported. In this latter species, the four phosphorus atoms of the two bidentate ligands describe the base of a pyramid with the NO group at the apex. The NO ligand completes the *penta*-co-ordination of the ruthenium atom. Distorted octahedral hydride complexes of both ruthenium and osmium with σ bonded naphthyl have also been studied by X-ray crystallography.[155,156]

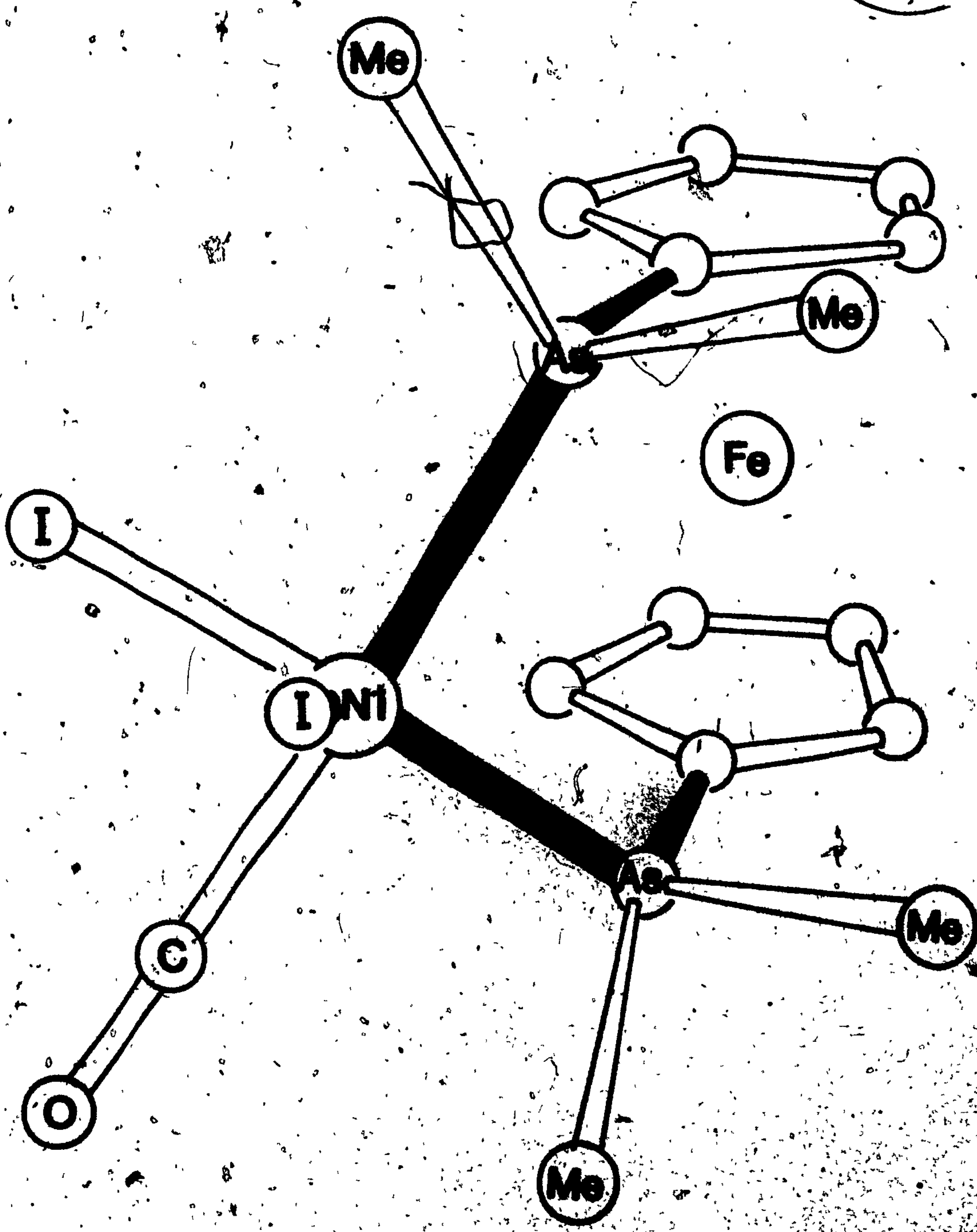
Sacco [157] has reported the only attempt at the reaction of $Co_2(CO)_8$ with a ligand of this type. An ionic complex postulated as $\{Co_2(CO)_4((C_6H_5)_2PCH_2CH_2(C_6H_5)_2)_3\}\cdot\{Co(CO)_4\}_2$ was isolated. A square planar complex of Rh(I) has been reported by Hall *et al*.[158] The X-ray structure determination of this complex $(Rh((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2)$ displayed a rhodium-phosphorus distance of 2.306Å.

Rhodium and iridium both form molecular oxygen cationic complexes with two $Ph_2PCH_2CH_2PPh_2$ ligands (where Ph abbreviates the phenyl group (C_6H_5)) in a relative *cis* configuration. The former complex acts as a reversible oxygen carrier but the latter does not display this characteristic. An X-ray crystallographic structure determination [134] of both species was undertaken to attempt an explanation of this difference. The hexafluorophosphate salts were prepared and their structure determined. In both complexes the molecular oxygen is π bonded, the two oxygen atoms occupying *cis*-octahedral sites. The phosphorus-carbon distances average 1.83(3)Å and the 'bite' (P-P distance) is 3.13 ± 0.03Å.

Nickel forms an interesting structure with an unusual ligand which is similar to the $R_2MCH_2CH_2MR_2$ ligand type. The complex diiodocarbonylferrocene-1,1'-bis(dimethylarsine)nickel(II) has been studied by X-ray crystallography.[137] The molecule is shown in Figure IV-A-1. The arsenic-arsenic distance is 3.036Å, compatible with the 'bite' for other ligands of this type. This ligand can adopt two different conformations.[159] In the first, the cyclopentadienyl rings are staggered and the two arsenics, the iron and the nickel atoms are co-planar. In the second, the two rings are eclipsed and this causes a steric strain which results in a deviation from co-planarity of the four above-mentioned atoms. The former conformation is favoured for larger metal atoms (arsenic-metal-arsenic angles much larger than 90°) whereas with smaller atoms, like nickel, the latter conformation is preferred (As-M-As angle of *ca.* 90°).

In the complex diiodocarbonylferrocene-1,1'-bis(dimethylarsine)nickel(II), the eclipsed conformation is indeed preferred as can be seen in Figure IV-A-1. The As-Ni-As

Figure IV-A-1. The molecular configuration of diiodo-carbonylferrocene-1,1'-bis(dimethylarsine)-nickel(II).


Me
Me
As
Fe
I
I
Ni
As
Me
C
O
Me

angle is 93.49(8)$^{\circ}$ and the Ni-As-C(cyclopentadienyl-substituted carbon) angles average 118.0(4)$^{\circ}$. This type of bonding pattern is as expected for the small nickel atom. The dihedral angles between the plane containing the nickel and the two arsenic atoms and the planes containing the arsenics and the cyclopentadienyl-substituted carbon atom of each ring average 45.6°.

Finally, two complexes of palladium with this type of ligand are worthy of mention. The complex $PdCl_2 \cdot (PhCH_3PCH_2CH_2PCH_3Ph)_2$[135] has a center of symmetry and a P-Pd-P bond angle of 85°. The average phosphorus-ethane carbon bond length was found to be 1.839(12)Å. Beran and Palenik[160] have reported a study of the linkage isomerization of thiocyanate complexes. The X-ray crystallographic structure determination of $Pd(Ph_2PCH_2CH_2PPh_2)(SCN)(NCS)$ revealed that one of the SCN moieties is bonded through the nitrogen atom and the other through the sulphur atom in this square-planar complex. A distinct *trans* influence is observed in this compound. The palladium-phosphorus distance (2.260(4)Å) *trans* to the isothiocyanate is longer than that *trans* to the thiocyanate (2.245(4)Å). This probably reflects the difference in the electronegativities of nitrogen and sulphur atoms.

Trans influence has also been observed in chromium and molybdenum carbonyl complexes with ligands of the type $(CH_3)_2MCFRCF_2M(CH_3)_2$ where M = P, As and R = H, CF_3. Four such complexes have been analyzed by X-ray crystallography.[161] In all complexes, the R group occupies an equatorial position with respect to the five-membered chelate ring. The C-C bond distances are unusually short (as low as 1.30Å) and this is explained in terms of an ionic contribution to the structures in which C=C character is required.

A full paper[162] has appeared on the X-ray structure determination of the complex $((CH_3)_2AsCHFCF_2As(CH_3)_2)\cdot Mo(CO)_4$. The As-Mo-As bond angle is 81.9°. The Mo-C (carbonyl) distances *trans* to each other average 2.02(1)Å whereas those *trans* to an arsenic atom average 1.98(1)Å. Cotton and Kraihanzel[163] have explained this in terms of the fact that carbonyl is a better π acceptor than As. Thus back-donation to a carbonyl carbon *trans* to As is expected to be greater than that *trans* to the carbonyl carbon with which it is competing. Thus the bond in the former case is shorter and stronger. The authors of the X-ray crystallographic study on $((CH_3)_2AsCHFCF_2As(CH_3)_2)Mo(CO)_4$ have also noted that the Mo-As distance is shorter than the sum of van der Waal's radii. According to them, this is due to back-donation of electrons from Mo to As ($d_\pi \rightarrow d_\pi$ bonding).

3. Complexes with $(CH_3)_2AsC{=}C(As(CH_3)_2)CF_2CF_2$

Cullen and Einstein have been actively involved in the study of iron and cobalt carbonyl complexes with the ligand tetrafluorocyclobutenebis(dimethylarsine), $(CH_3)_2AsC{=}C(As(CH_3)_2)CF_2CF_2$ (abbreviated ffars). Cullen has recently published a review [164] on these compounds. We shall first examine the iron-ffars complexes. Subsequently we shall review the cobalt carbonyl complexes more thoroughly from a structural point of view.

The ffars ligand is perhaps the most versatile of all the bidentate chelating ligands discussed in this Introduction. For example, the ligand has been shown to bridge two iron atoms, act as a bidentate chelate with one iron and behave as a monodentate ligand also with iron.

By the ultraviolet irradiation of a solution of $Fe_3(CO)_{12}$ and ffars, [165] the product $Fe_3(CO)_{10}$(ffars) was recovered and subjected to single crystal X-ray structure determination.[166] The complex is such that the two equatorial carbonyls on the equivalent iron atoms in $Fe_3(CO)_{12}$ have been replaced by the diarsine. The ligand is thus spanning an Fe-Fe bond (2.522(7)Å) with an arsenic-arsenic 'bite' of 4.08Å. This bridge does not seriously affect the Fe-Fe bond length (2.56(1)Å in the parent $Fe_3(CO)_{12}$ [167]).

The complex $Fe_2(CO)_6$(ffars) has been examined structurally by Einstein and Trotter.[168] In this complex the diarsine does not span an iron-iron bond. Rather, the ligand acts as a bidentate chelate to one $Fe(CO)_3$ unit (As-Fe-As angle of 86°) whereas the other $Fe(CO)_3$ unit appears to π bond to the olefinic carbon-carbon linkage. The ligand is bent in this complex (probably due to the unusual bonding mode) and the two iron atoms are separated by 2.88Å, which is rather long compared to the average Fe-Fe (non-bridged) distance of 2.67Å in $Fe_3(CO)_{12}$.[167]

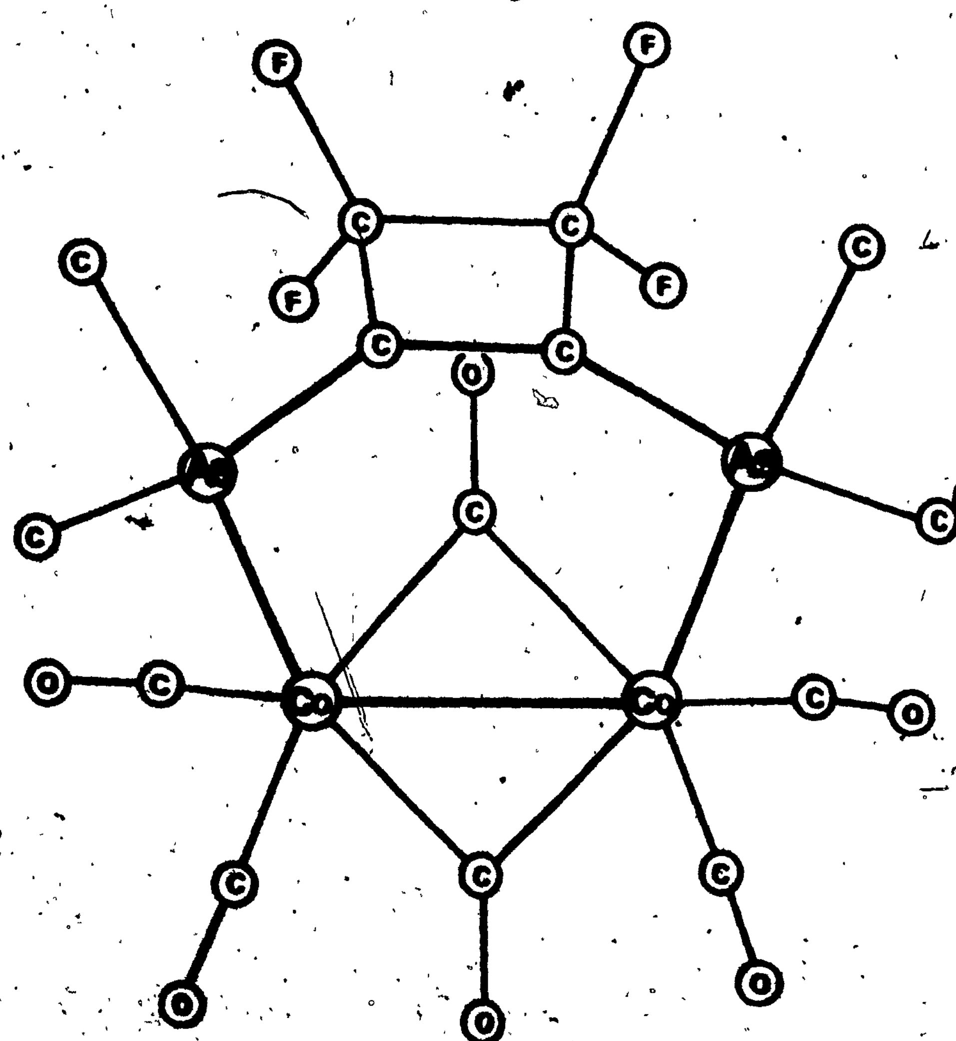
Finally, the ffars ligand (or rather a modified version thereof) can also act as a monodentate 'dangling ligand'. Indeed the reaction of $Fe(CO)_5$ with $Ph_2P\overline{C{=}C(As(CH_3)_2)\cdot CF_2}CF_2$ has resulted in the replacement of one carbonyl with the ligand bonded through the phosphorus atom.[169] The preference for bonding through phosphorus cannot be due to electronegativity differences between As and P (they are essentially the same), nor to steric crowding which would have favoured arsenic. The explanation given is that the presence of the phenyl groups on the phosphorus atom enhances the $d_\pi \rightarrow d_\pi$ bonding from filled d orbitals of iron to the empty phosphorus d orbitals.

The ffars ligand has also been observed to split at an arsenic-carbon (olefinic) bond. When this happens, the $As(CH_3)_2$ moiety acts as a bridge between the iron atoms and the $(CH_3)_2AsC{=}CCF_2CF_2$ residue does the same. The latter unit also bonds to an iron atom through a π interaction. Thus complexes of the general form $Fe_3(CO)_9 \cdot (R_2AsC{=}CCF_2CF_2)(AsR_2)$ have been synthesized and studied by X-ray crystallography.[140,170,171]

The ffars ligand has been shown to span a cobalt-cobalt bond in four complexes which have been studied by X-ray crystallography. $Co_2(CO)_6(CH_3)_2AsC{=}C(As(CH_3)_2)CF_2CF_2$ has been synthesized and subjected to structure analysis.[172,173] A schematic representation of the complex can be see[illegible] Figure IV-A-2. This compound can be said to be de[illegible] from dicobaltoctacarbonyl by replacement of a terminal carbonyl ligand from each cobalt atom with the bidentate ligand. Thus the two bridging carbonyl ligands remain. The cobalt-cobalt bond, triply bridged, is 2.483(4)Å. The 'bite' is 4.064Å. The cobalt-arsenic distances are 2.339(4) and 2.336(4)Å respectively, quite amenable with the sum of Pauling's metallic radius for Co (1.16Å) and the covalent radius of As (1.18Å). The Co-C (carbonyl) bond lengths range from 1.91(2) to 1.95(2)Å for bridging groups and from 1.79(3) to 1.83(3)Å for the terminal carbonyls.

By heating this complex in hexane, a rearrangement product has been obtained[174] which involves the dimerization of the cyclobutene residues. The two liberated dimethylarsine residues each link two cobalt atoms.

Figure IV-A-2. A schematic representation of the molecular geometry of tetrafluorocyclobutene-bis-(dimethylarsine)hexacarbonyldicobalt(0).


F
F
C
C
F
F
C
C
C
O
C
As
As
C
C
C
O
C
Co
Co
C
O
C
C
C
O
O
O

The first cobalt atoms each have three terminal carbonyl ligands and they themselves link the aforementioned dimethylarsino moiety (Co-As: 2.391(5)Å) with a similar moiety on the dimerized cyclobutene (Co-As: 2.323(6)Å). The second cobalt atoms are linked by a metal-metal bond (2.450(9)Å) and a carbonyl bridge and each carries a terminal carbonyl ligand. There are also π interactions between the olefinic bonds in the dimerized ligand and each of these latter cobalt atoms.

The ffars ligand has also been recently shown to form bridging complexes with cobalt clusters. The crystal structure of ethylidyneheptacarbonyl-μ-{1,2-bis-(dimethylarsino)tetrafluorocyclobutene}-*triangulo*-tricobalt has been reported.[175,176] In this complex, originating from $CH_3CCo_3(CO)_9$ with ffars, the ligand can be thought of as replacing two terminal carbonyls, one on each cobalt. A carbonyl bridge is present. The two Co-Co bonds which are not bridged by the ligand are 2.479(2) and 2.470(2)Å whereas that which is bridged is 2.440(1)Å. The cobalt-arsenic distances average 2.347(2)Å. The sum of the covalent radii is 2.342Å.

If the complex $CF_3CCo_3(CO)_9$ is treated with ffars,[175] a rearrangement occurs and a tetrahedron of cobalt atoms is formed with two diarsine ligands bridging alternate sides. An X-ray crystallographic structure determination of di-μ-{1,2-bis(dimethylarsino)tetrafluorocyclobutene}-

octacarbonyl-*tetrahedro*-tetracobalt[177] revealed that there were weak but significant interactions between some carbonyl groups and adjacent non-bonded cobalt atoms (Co-C-O angles of 159, 161 and 159°). The complex is devoid of bridging carbonyl groups. Crystallographic symmetry restrictions afford but one determined bridged Co-Co distance (2.446(2)Å) and two unbridged analogs (2.343(2) and 2.510(2)Å). The differences seem random. The average As-Co distance is 2.274(4)Å, considerably shorter than the sum of covalent radii for As and Co. These unusual features may all be due to the carbonyl-cobalt interactions or perhaps they can be attributed to the fact that the complex does not possess bridging carbonyl ligands.

4. Complexes with *o*-phenylenebis(dimethylarsine)

The best known of the diarsine ligands is likely *o*-phenylenebis(dimethylarsine) (diars). A summary of the ligands of this type that exist has been published.[178] Feltham and Silverthorn[179] have published a paper in which they claim that there is no spectroscopic evidence for $d_{\pi} \leftarrow d_{\pi}$ bonding between the metal and the diars ligand in complexes of Cr, Co and Fe in their higher oxidation states.

Nickel,[138] gold[139] and cobalt[138] all form *trans*-bis-(*o*-phenylenebis(dimethylarsine)) dihalogen cationic complexes which have been studied by X-ray crystallography. The ligand in all these complexes acts as a bidentate chelate. In both the cobalt and nickel complexes, the plane of the substituted phenyl ring makes an angle of 9° with that of the two arsenic atoms and the metal. In the gold diiodo-iodide salt, however, the angle is 28°. For the cobalt chloride salt, the As-Co-As angle is 86.6° and the cobalt-arsenic bond length 2.334(3)Å. Similar results (88.0(1)° and 2.341(6)Å respectively) were obtained from a single crystal X-ray crystallographic structure determination of the perchlorate salt of the same cation.[180]

Another complex of cobalt with diars has been synthesized and its structure determined by X-ray crystallography.[181] Bis-(*o*-phenylenebis(dimethylarsine))-cobalt(II) perchlorate shows two equivalent 2.30(1)Å Co-As bond lengths and an As-Co-As angle of 86.2(4)° for the crystallographically-unique part of the cation.

5. Complexes with Other Bidentate Chelating Ligands

Bidentate ligands with longer carbon chains between the *sigma* donor atoms have been synthesized and complexes have been studied. The complex tris(dimethylarsinopropyl)phosphine cyanonickel perchlorate has been investigated crystallographically.[182] The nickel displays a trigonal bipyramidal configuration with the phosphorus atom occupying an axial site and the cyanide occupying the other axial site. The distance between the arsenic atoms is now sufficient for the ligand to span the equatorial (120^{o}) sites.

In the complex $Ni(Ph_2PCH_2CH_2OCH_2CH_2PPh_2)Cl_2$, the ligand occupies two sites of a tetrahedral nickel environment.[183] When the ligand is further lengthened, a *pseudo*-square planar geometry is preferred with the ligand now spanning a *trans* configuration.[184] The P-Ni-P angle in $Ni(Ph_2PCH_2CH_2OCH_2CH_2OCH_2CH_2PPh_2)I_2$ is 162^{o}.

6. Complexes with $R_2MCH_2MR_2$

Complexes with ligands of the general form $R_2MCH_2MR_2$ have received relatively little attention although some X-ray crystallographic studies have recently appeared. When M = phosphorus, a complex $Mo(CO)_4(Ph_2PCH_2PPh_2)$ has been synthesized and an X-ray structure determination has been accomplished.[185] The co-ordination about the molybdenum is distorted octahedral, the P-Mo-P angle measuring 67.3(1)^{o}. The $\overline{Mo-P-C-P}$ ring was planar with an average Mo-P-C angle of 96.9(3)^{o} and a P-C-P angle of 95.6(4)^{o}. The Mo-P bond length was shorter than generally accepted for a single bond and this was attributed to $d_\pi \rightarrow d_\pi$ back-bonding. The Mo-C (carbonyl) bond *trans* to a phosphorus atom (1.93Å) was found to be shorter than that *trans* to a carbonyl (2.04Å). It was claimed that this was also a result of $d_\pi \rightarrow d_\pi$ back-bonding.

A complex bis{bis(dicyclohexylphosphino)-methane}nickel was studied[136] and the two Ni-P-C-P ring systems were again found to be planar. The phosphorus-methylene carbon bond length averaged 1.864(6)Å and the P-C-P angle was 96.4(3)°. The Ni-P-C angles averaged 92.9(2)°. The cyclohexyl substituents were in the chair conformation.

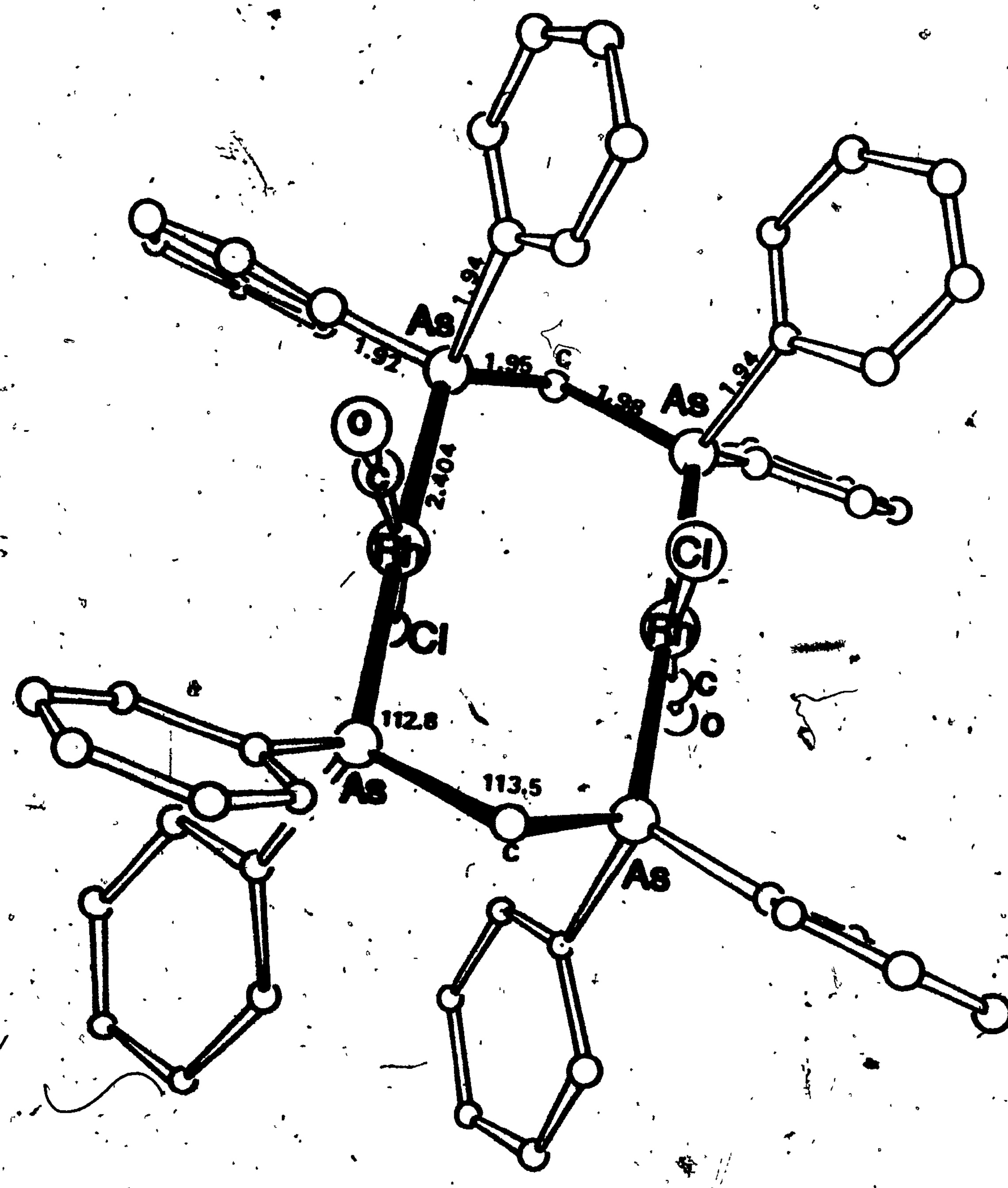
The ligand bis(diphenylarsino)methane has been found, in a molybdenum seven-co-ordinate capped octahedral complex, $Mo(CO)_2(Ph_2AsCH_2AsPh_2)_2Br_2$, to be both monodentate and bidentate.[186,187] The monodentate ligand is 'dangling', the Mo-As distance showing some degree of double bond character. It was pointed out that in the complex $Mo(CO)_4(Ph_2PCH_2PPh_2)$, the four-membered ring was planar. The bidentate ligand in the complex $Mo(CO)_2(Ph_2AsCH_2AsPh_2)_2Br_2$ is bent about the line joining the two arsenic atoms. The 'bite' is 2.88Å whereas the As-As distance in the 'dangling' ligand is 3.28Å. In the bidentate ligand, the Mo-As-C angles average 98° whereas the angle at the methylene carbon is 90°. In the monodentate diarsine, this angle is 116.5°. The angle As-Mo-As is 66.7(2)°.

Steric strain is said to be responsible for the bend in the bidentate ligand. The dihedral angle between the plane described by the molybdenum and the two arsenics and the plane described by the methylene carbon and the two arsenics is 68^{o}. The average As-C (phenyl) distance is 2.03Å and the average As-C (methylene) distance is 1.97 ± 0.03Å. The crystal structure of a tungsten complex, $W(CO)_3(Ph_2AsCH_2AsPh_2)_2Br_2$, made in a similar fashion, was also reported.[186] In this complex, both diarsine ligands act as monodentates.

The ligand bis(diphenylarsino)methane has also been shown to bridge two transition metals in the complex $((C_6F_5)_2Hg)_2(Ph_2AsCH_2AsPh_2)$.[188] There exists a crystallographic two-fold axis at the methylene carbon which relates the two halves of the molecule. The As-C-As angle is $113(3)^{o}$ whereas the As-C (methylene) distance is 2.01(5)Å.

In none of the above cases has the ligand been shown to bridge a metal-metal bond. The only compound that <u>might</u> display this type of bonding was studied using the techniques of X-ray crystallography by J.T. Mague.[189,190] The Rh-Rh distance in the compound di-μ-bis(diphenylarsino)-methane-bis(*trans*-chlorocarbonylrhodium(I)), shown in Figure IV-A-3, is 3.396Å and it is dubious whether this constitutes a metal-metal bond at all. It is preferable to state that the complex consists of two Rh(CO)Cl units held together by two diarsine ligands.

Figure IV-A-3. The molecular configuration of the complex $(RhCl(CO)(Ph_2AsCH_2AsPh_2))_2$.


As
1.94
1.92
1.95
C
1.98
As
1.94
O
C
2.404
Rh
Cl
Cl
Rh
C
O
112.8
As
113.5
C
As

The As-C-As bond angle of 113.5(4)^{o} affords a rather large 'bite' (3.29Å) for the ligand in this complex. The ligand is again bent (along the line joining the arsenic atoms), the dihedral angle between the plane containing the two arsenics and the methylene carbon and the plane containing the two arsenics and the two rhodium atoms is 54.3^{o}. Other relevant bond lengths and angles are given on Figure IV-A-3.

As yet there has been no report of the crystallographic structure determination of a cobalt complex of bis(diphenylarsino)methane or bis(diphenylphosphino)methane. In the light of the previous discussion, the type of bonding (monodentate, chelating or bridging) is of some interest. The research work reported in this chapter involves the structures of two complexes which have an acetylenic linkage (diphenylacetylene) instead of the two bridging carbonyl ligands. These linkages have been reviewed in Chapter III, Section A and it was considered appropriate to close this introduction with a study of various structural reports of diphenylacetylene complexes of transition metals.

7. Complexes with Diphenylacetylene

Gusev and Struchkov have published a review,[191] a large portion of which is dedicated to the structure of π-acetylene complexes. The importance of the structure determinations of these complexes is stated in relation to the elucidation of the nature of π bonding and the mechanisms of catalysis using acetylenes. The authors concentrate their efforts on diphenylacetylene complexes of niobium although compounds with other transition metals are mentioned.

There are, according to these authors, five general structural features of these π-acetylenic complexes. The complexed triple bond is elongated as compared to the value of 1.205Å[192,193] found in the free ligand. Second, the ligand is no longer linear but the two acetylenic substituents are bent away from the bonding site. Probably as a consequence of the ensuing steric repulsions, there occurs a twisting about the C≡C bond. Fourth, the metal atom which co-ordinates to the acetylenic ligand gains the number of electrons necessary to achieve an 18 electron shell. Finally, there is an appreciable shortening (0.2 - 0.4Å) of the metal-to-acetylenic carbon distance in comparison to a single M-C bond distance.

The first structure determination on a diphenylacetylene-transition metal complex was described in Chapter III, Section A. Sly's paper [77] on μ-diphenylacetylenehexacarbonyldicobalt reports a complexed C≡C distance of 1.46Å which was subsequently revised [78] to 1.369Å. The phenyl-C≡C angles average 138° and the cobalt-acetylenic carbon distances average 1.96Å. The cobalt-cobalt distance is 2.47Å.

The phenyl rings in the complex make an angle of 62° with each other and this is commensurate with the 60° angle obtained for the complex bis(cyclopentadienyl)-μ-diphenylacetylenedinickel.[194] The average phenyl-C≡C angle is 140° in this complex and the C≡C complexed bond distance is 1.35(3)Å.

Very recently, the crystallographic structure determination of the complex $W(O)\pi-(C_5H_5)\sigma-(C_6H_5)\cdot$(PhC≡CPh) has been published.[195] The complex was synthesized by the ultraviolet irradiation of a solution of $W(CO)_3\pi-(C_5H_5)\sigma-(C_6H_5)$ and PhC≡CPh. The average phenyl-C≡C angle was 143° and the C≡C distance 1.29Å. In this complex, the acetylene is bonded to but one metal atom. The dihedral angle between the two phenyl ring planes is 57° and the torsional angle around the C≡C bond is very small (2°). Three moles of diphenylacetylene react with one mole of $W(CO)_3(CH_3CN)_3$[196] to give the complex $W(CO)(PhC{\equiv}CPh)_3$ which has been studied by X-ray crystallography.[117,197] The C≡C distances average 1.30Å, and the phenyl-C≡C angles 140°. The dihedral angle between the phenyl rings is not quoted. R.B. King[198] had correctly predicted the nature of this complex four years before the crystal structure was reported.

Palladium has been shown to form the complex μ-diphenylacetylene-bis-(π-pentaphenylcyclopentadienyl)-dipalladium(I)[199] in which the acetylenic ligand bridges a palladium-palladium bond in much the same way as it bridges a Ni-Ni bond. The C≡C bond length is 1.33Å. The relative configuration of the phenyl groups is not reported in this communication.

The series of three X-ray crystallographic structure determinations of diphenylacetylene-niobium complexes includes two complexes $Nb(CO)(\pi\text{-}C_5H_5)(Ph_2C_2)(\pi\text{-}Ph_4C_4)$[200,201] and $Nb(CO)(\pi\text{-}C_5H_5)(Ph_2C_2)_2$[202,203] in which the diphenylacetylene ligand is bonded to a unique niobium atom. The C≡C bond is 1.26Å in the former and 1.35Å in the latter complex. The phenyl-C≡C angles average 140^{o}. The third complex is $((\pi\text{-}C_5H_5)Nb(CO)(Ph_2C_2))_2$[204] which contains a Nb-Nb bond. The bridging ligand exhibits a C≡C bond length of 1.39Å and a phenyl-C≡C angle of 130^{o}. Again the relative configurations of the two phenyl rings are not given.

SECTION B. EXPERIMENTAL

1. The Source of the Complexes Studied

For full details on the preparation and characterization of a) μ-{bis(diphenylarsino)methane}-μ-(diphenylacetylene)tetracarbonyldicobalt(0); $Co_2(CO)_4 \cdot (PhCCPh)(Ph_2AsCH_2AsPh_2)$, b) μ-{bis(diphenylphosphino)-methane}-μ-(diphenylacetylene)tetracarbonyldicobalt(0); $Co_2(CO)_4(PhCCPh)(Ph_2PCH_2PPh_2)$ and c) the di-μ-{bis(diphenylarsino)methane}-μ-(diphenylacetylene)dicarbonyldicobalt(0)· 1,2-dichloroethane solvate complex; $Co_2(CO)_2(PhCCPh) \cdot (Ph_2AsCH_2AsPh_2)_2 \cdot H_2ClCCClH_2$, the reader is referred to the soon-to-be-presented Doctoral Thesis of Mr. David N. Hall. It is the intention here to present but a short summary of the origin of these complexes and whatever physical data might be relevant to their X-ray crystallographic structure determination.

μ-{bis(diphenylarsino)methane}-μ-(diphenylacetylene)tetracarbonyldicobalt(0) was prepared by the reaction, in refluxing hexane, of 1 mole of diphenylacetylene-hexacarbonyldicobalt(0) with 1 mole of bis(diphenylarsino)-methane. The complex was recrystallized from hexane to give the crystals used in the structure analysis. Di-μ-{bis(diphenylarsino)methane}-μ-(diphenylacetylene)dicarbonyldicobalt(0) was prepared by refluxing 2 moles of bis(diphenylarsino)methane with 1 mole of diphenylacetylenehexacarbonyl-dicobalt(0) complex in benzene solution. The wine-red solid so obtained was recrystallized from 1,2-dichloro-ethane. Finally, μ-{bis(diphenylphosphino)methane}-μ-(diphenylacetylene)tetracarbonyldicobalt(0) was synthesized just as for the arsenic analog except that the phosphorus precursor was used. Recrystallization was from hexane solution.

2. The Attempted Solution of the X-ray Crystallographic Structure of μ-{bis(diphenylarsino)methane}-μ-(diphenylacetylene)tetracarbonyldicobalt(0)

A crystal, of approximate dimensions 0.1 x 0.2 x 0.1 mm (recrystallized from hexane by cooling), was mounted on a eucentric goniometer head and the height was adjusted on the diffractometer goniometer. The zero level Weissenberg photograph showed orthorhombic symmetry. In the first level Weissenberg, the right-left symmetry was maintained about one axis but disappeared about the second. The latter showed twice as many spots on the first level as were observed on the zero level axis. This zero level axis was labeled b^* and the second axis was arbitrarily called c^*. The monoclinic crystal was assumed to be mounted on a.

The $hk0$ monoclinic zone was obtained using the precession camera. The $h0l$ zone showed a diamond pattern that was absent on the $h1l$ zone. The space group was assigned as $P2_1/n$ (non-standard setting of $P2_1/c$, No. 14). The extinction conditions for this space group are a) on $h0l$, $h + k = 2n + 1$ and b) on $0k0$, $k = 2n + 1$.

The unit cell parameters were computed from the film-measured y_n distances. For this crystal, the measured values were $y_a = 1.89$ mm, $y_b = 2.00$ mm, $y_c = 2.62$ mm and $\beta^* = 85.5^{\circ}$. This gives, according to Equation II-B-1, $a^* = 0.0443^{225}$, $b^* = 0.0469^{821}$ and $c^* = 0.061^{4418}$ Å^{-1}. From the monoclinic conversion equations,[124] $a = 22.63$, $b = 21.32$, $c = 16.33$ Å, $\beta = 94.5^{\circ}$. The goniometer was then mounted on the diffractometer and the (0,10,0) and (0,0,8) reflections were located and centered. The third axis reflection (the (6,0,0)) was found and centered. Twelve reflections were centered at plus and minus 2θ. They are the (14,0,0),(-14,0,0),(10,10,0),(10,-10,0),(-10,10,0), (-10,-10,0),(10,0,-6),(-10,0,6),(12,0,6),(-12,0,-6),(0,0,10) and (0,0,-10). Two cycles of least squares refinement of the cell parameters using these reflections gave the final values of $a = 22.394 \pm 0.005$, $b = 21.492 \pm 0.007$, $c = 16.168 \pm 0.005$ Å and $\beta = 94.50 \pm 0.02^{\circ}$. The unit cell volume was thus 7757.4 Å^3. Based on this volume and a formula weight of 880 g mole^{-1} for $Co_2As_2C_{43}H_{32}O_4$, the calculated density for 4 molecules in the unit cell is 0.754 g cm^{-3}. With two molecules in the asymmetric unit, the calculated density is 1.507 g cm^{-3}. The observed density, measured by flotation in zinc iodide aqueous solution, was 1.47^{5} g cm^{-3}. The molecular volume, based on eight molecules per unit cell, was 969.7 Å^{3}.

Data collection was carried out using the parameters summarized in Table IV-B-1. Planes were collected in one-quarter of the sphere with positive h and k. There were 7469 reflections measured of which 1396 were absent and 1679 were less than 3σ. Thus 4394 reflections were accepted. Absorption corrections were not applied to the observed data. The linear absorption coefficient μ was 25.1 cm^{-1}.

NORMA was used to calculate normalized structure factors E_{hkl}. Of the 4394 reflections processed, 1410 had E_{hkl} values greater than 1.0, 117 had values E_{hkl} greater than 2.0 and finally, 3 had E_{hkl} greater than 3.0. A value of 1.80 was chosen for the minimum E value and *REL* was used to attempt phase solution. Two hundred reflections only were available of which only 20 on the average had phases which were considered determined. Consistency indices varied from 0.01 to 0.05 for this attempt. On examination of the starting set, the four seminvariants were not as random as they should have been. Indeed, the k index of all four was 5 and the h index was 0 for the first two and 4 for the other two. Another attempt at

TABLE IV-B-1

DATA COLLECTION PARAMETERS FOR

$Co_2(CO)_4(PhCCPh)(Ph_2AsCH_2AsPh_2)$

Radiation used:		Mo K_α (λ = 0.71069Å)	
Pulse height analyzer		100%	
Upper level		6.0	
Lower level		2.0	
Attenuators		Used	
Space group routine used:		$P2_1/n$	
maximum h:	23	minimum h:	0
maximum k:	23	minimum k:	0
maximum l:	16	minimum l:	−16
maximum 2θ:	40.0°	mimimum 2θ:	4.0°
Standards used (hkl)		(8,0,0)* (0,10,0) (0,0,6)	
Value and variation		41815 ± 15%	
Interval		every 50 reflections	
Background		40 second counts	
Base length of scan		2.0°	
Total number of reflections collected:		7469	

* This standard was used for scaling.

statistical phasing was made.

Care was taken to avoid the relationship of *h*,*k* and *l* of the starting set that had plagued the first try. A reasonable starting set was obtained which included the reflections (4,5,-9), (5,11,1), (9,6,-1), (4,14,-1), (3,12,-2), (2,1,1) and (9,6,1). The *NBACK* option was 1 for the first pass and 0 for the second. The minimum value of *E* was reduced to 1.65 thus allowing for a greater number (303) of reflections to be used. *PROB1* was set at 0.85 and *PROB2* was 0.70. *PROBK* was 0.07. Consistency indices, *C*, varied from 0.52 to 0.78. Two solutions were prepared and used to calculate electron density maps but both attempts were unsuccessful. The first solution, with the highest consistency index (0.78) gave 151 pluses and 143 minuses phased in 5 cycles. The second had a consistency index of 0.66 with 140 pluses and 143 minuses in 5 cycles. In neither case did the signs predicted for the starting set change from cycle to cycle. Both solutions gave *E*-maps which, when drawn up, gave no recognizable pattern. The strong peaks were used in several structure factor calculations but the discrepancy factors were too high to imply a correct solution.

The heavy-atom method was also tried in order to solve the phase problem. A sharpened Patterson function was calculated using half-angstrom resolution. The map was a view down the c axis of the monoclinic real cell. The equivalent positions in $P2_1/n$ are 1) x,y,z 2) $-x,-y,-z$ 3) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$ and 4) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$. The vectors between these equivalent positions are summarized in Table IV-B-2. The origin peak was 999 and the arsenic-arsenic vector should thus have an intensity of 25. The intensity of the cobalt-cobalt vector must be 17. Peaks were found on the Harker line and the Harker section but the intensities were much higher than predicted for single vector peaks due to accidental overlap. A surfeit of peaks caused considerable difficulty and after many weeks of exhaustive peak selection and verification, the efforts seemed futile.

Another map was computed (unsharpened) based on high angle data only. If the reflection had a value of $(\text{sine}\theta)/\lambda$ less than 2.245, it was not used in the Patterson summation. The aim here was to phase the data based on reflections contributed to in a greater proportion by the heavy atoms in the cell. The effort was to no avail since similar overlap of vectors occurred . The attempt at solution of this structure was terminated at this point.

TABLE IV-B-2

PATTERSON VECTORS FOR A SINGLE ATOM IN

$Co_2(CO)_4(PhCCPh)(Ph_2AsCH_2AsPh_2)$

Vector	Multiplicity
$\pm(2x, 2y, 2z)$	1
$\pm(\frac{1}{2}, \frac{1}{2}+2y, \frac{1}{2})$ Harker Line	2
$\pm(\frac{1}{2}+2x, \frac{1}{2}, \frac{1}{2}+2z)$ Harker Section	2

3. <u>The Crystal and Molecular Structure Determination of μ-{bis(diphenylphosphino)methane}-μ-(diphenylacetylene)-tetracarbonyldicobalt(0)</u>

A crystal of the complex was recrystallized from hexane. The 0.2 x 0.2 x 0.2 mm roughly cubic crystal was investigated by Weissenberg and precession geometry. The zero and first level Weissenberg as well as zero and first level a^*c^* and b^*c^* precession photographs indicated the space group was $P2_1/n$. The monoclinic crystal was assigned to be mounted on the c axis in this structure.

The film-measured distances were $y_a = 3.53$, $y_b = 2.08$ and $y_c = 2.76$ mm. This gave (Equation II-B-1) reciprocal cell dimensions of $a^* = 0.082^{7834}$, $b^* = 0.0486^{616}$, $c^* = 0.064^{6086}$ Å^{-1} and a measured β^* angle of 82.3°. Thus $a = 12.19$, $b = 20.55$, $c = 15.62$ Å and $\beta = 97.7°$.

The (6,0,0) and (0,16,0) reflections were located and centered. Using the approximate cell parameters measured from film and the ω, χ and φ angles of these two reflections, the (0,0,10) reflection was found and centered. Twelve reflections (9,0,-3), (-9,0,3), (1,0,11), (-1,0,-11), (0,16,0), (0,-16,0), (-1,12,7), (1,-12,-7), (-7,0,11), (7,0,-11), (14,0,5), (14,0,-5) were centered at both plus and minus 2θ, the results were averaged and they were used in three cycles of least squares to give an orientation matrix and the refined cell parameters $a = 11.97 \pm 0.02$, $b = 20.41 \pm 0.02$, $c = 15.45 \pm 0.02$Å, $\beta = 97.57 \pm 0.07^{\circ}$. The unit cell volume was thus $3742.^{5}$Å^3 giving a molecular volume of $935.^{6}$Å^3 for $Z = 4$.

The observed density, measured by flotation in zinc iodide water solution was 1.35(2) g cm^{-3}. The density calculated from the measured volume, a formula weight of 792.5 and four molecules in the unit cell, was 1.40^{6} g cm^{-3}.

Data collection was carried out using those parameters described in Table IV-B-3. Of the total of 3942 reflections collected, 518 were absent and 280 were less than 3σ. Thus 3144 were accepted and used in least squares refinement. Absorption corrections were not applied and they were probably not warranted ($\mu = 10.49$ cm^{-1}).

The heavy-atom method was used with great success to solve the phase problem. A sharpened Patterson was computed using the thermal parameter (3.25) and the scale factor (1.299) predicted by *PREP*. One-half angström resolution was chosen for computation of a full unit cell of vector space which had its origin at the center.

The vector set is described in Table IV-B-2 for $P2_1/n$. Examination of the Harker line gave two peaks, one centered at -0.170 and the other at -0.310. Both had

TABLE IV-B-3

DATA COLLECTION PARAMETERS FOR $Co_2(CO)_4(PhCCPh)(Ph_2PCH_2PPH_2)$

Radiation used:	Mo K_α (λ - 0.71069Å)
Pulse height analyzer	100%
Upper level	6.0
Lower level	2.0
Attenuators	Used
Space group routine used:	$P2_1/n$
maximum *h*: 11	minimum *h*: -11
maximum *k*: 19	minimum *k*: 0
maximum *l*: 14	minimum *l*: 0
maximum 2θ: 40.0°	minimum 2θ: 4.0°
Standards used *(hkl)*	(6,0,0) (0,6,0) (0,0,10)
Value and variation for scaling	77415 ± 15%
Interval	every 50 reflections
Background	40 second counts
Base length of scan	2.1°
Total number of reflections collected:	3942

intensities of approximately 250. The theoretical intensity for a Co-Co vector is 215. Since both these peaks were at a Patterson position of $\frac{1}{2} + 2y$, where y is the real cell position, these equations were solved for y and values of -0.335 and -0.405 respectively were obtained. The two large peaks found on the Harker section are given in Table IV-B-4. Two compatible sets of co-ordinates were found (multiplicity of $2x$, $2y$, $2z$ peak is one-half that of the Harker peaks (Table IV-B-2)) and these were refined in an isotropic least squares cycle (ISO1) using *SFLS-5*.

The discrepancy index R before refinement was 57.2% for 3144 reflections. The scale factor changed by about 15% in this cycle and the isotropic thermal parameters, which were put in as 3.0 for both Co1 and Co2, dropped to 0.1 and 0.4 respectively. The R factor was 49.9% after this refinement cycle and an observed Fourier map was calculated based on this improved model. Here one-third angström resolution was taken. This permitted the identification of peaks for the two phosphorus atoms, the acetylenic carbons, the carbonyl atoms and most carbon atoms in four of the six rings.

The discrepancy factor dropped from 36.1% to 25.2% in a cycle of refinement (ISO2) of the positional and isotropic thermal parameters of these atoms. A difference Fourier (*RMAX* = 4.19) permitted the location of all remaining

TABLE IV-B-4

THE HEAVY ATOM METHOD ANALYSIS OF THE PATTERSON FOR $Co_2(CO)_4(PhCCPh)(Ph_2PCH_2PPh_2)$

Patterson Peak Intensity	$\frac{1}{2} + 2x$	$\frac{1}{2} + 2y$	x	z	y	$\pm 2x, \pm 2y, \pm 2z$	Intensity
Between 167 & 176	-0.080	0.160	-0.290	-0.170	-0.335	(-0.580,-0.670,-0.340)	
						0.420, 0.330,-0.340	- - -
					-0.405	(-0.580,-0.810,-0.340)	Co1 - Co1
						0.420, 0.190,-0.340	134
266	-0.220	0.380	-0.360	-0.060	-0.335	(-0.720,-0.670,-0.120)	Co2 - Co2 Between 106 & 98
						0.280, 0.330,-0.120	
					-0.405	(-0.720,-0.810,-0.120)	
						0.280, 0.190,-0.120	- - -

Co1: $x_1 = 0.290$ $y_1 = 0.405$ $z_1 = 0.170$

Co2: $x_2 = 0.360$ $y_2 = 0.335$ $z_2 = 0.060$

244 $(x_1 - x_2) = -0.070$ $(y_1 - y_2) = 0.070$ $(z_1 - z_2) = 0.110$ Co1 - Co2

non-hydrogen atoms. Two further cycles (ISO3 and ISO4) of isotropic least squares refinement with 205 parameters in one matrix brought the discrepancy index from 17.0% to 10.8% with a "goodness-of-fit" parameter of 7.025. At this stage, the rigid ring approximation was introduced and the structure was refined using the program *NUCLS4*.

The six phenyl rings were assigned a center of mass, orientation angles ϕ, θ and ρ and an isotropic thermal parameter for each atom. Isotropic refinement was continued for two cycles as described in Table IV-B-5. Then four cycles of anisotropic refinement on the six rings gave a final discrepancy factor of 8.8% and a final weighted discrepancy factor of 10.2%. Anomalous dispersion corrections were applied to the cobalt atomic scattering factors ($\Delta f' = 0.40$, $\Delta f'' = 1.10$).

No attempt was made to locate the hydrogen atom positions on the final difference Fourier. This map gave a $\Delta e Å^{-3}$ maximum of 0.9 and confirmed that the cell was devoid of solvent molecules. The 32 hydrogen atom positions were calculated using a carbon-hydrogen bond length of 0.98 Å.

All positional and thermal parameters can be found in Appendix B. The positional parameters for the rigid ring carbon atoms have been calculated from the center of mass and the directional angles of the rings. The C-C

TABLE IV-B-5

STRUCTURE FACTOR INFORMATION FOR $Co_2(CO)_4(PhCCPh)(Ph_2PCH_2PPh_2)$[a]

	AFTER ISO(4)	ISO(5)	ISO(6)	ANISO (1)	ANISO (2)[b]	ANISO (3)	ANISO (4)
Scale Factor	2.0717	2.0744	2.0755	2.0839	2.0856	2.0674	2.0679
Total # of parameters		133	133	208	208	208	208
Number of Reflections	3144	3144	3144	3144	3144	3144	3144
"Goodness-of-fit"	9.06	6.73	6.71	5.88	5.93	5.86	5.86
R	14.4	10.4	10.4	8.9	8.8	8.8	8.8
R_w	16.0	11.9	11.9	10.3	10.4	10.2	10.2

a The structure factor calculation data listed is for that run immediately AFTER the least squares refinement cycle heading the column.

b Anomalous dispersion corrections were introduced at this point (see text).

bond lengths are all 1.390 Å and the angles 120°. The isotropic thermal parameters are as refined by *NUCLS4*. The final structure factor calculation did not include the hydrogen atoms since the number of atoms possible in *NUCLS4* would not allow it.

The 3144 reflections used in the refinement are listed in Appendix B along with their F_{obs} and F_{cal} values. A reject routine was not used in the refinement. The final shifts in the parameters were, at the most, 0.1 of their estimated standard deviations. Final positional and thermal parameters can also be found in Appendix B along with the equations of the planes of the six phenyl rings of the structure.

4. <u>The Crystal and Molecular Structure of the Di-μ-{bis(diphenylarsino)methane}-μ-(diphenylacetylene)-dicarbonyldicobalt(0)·1,2-dichloroethane solvate</u>

Oscillation photographs, recorded using a crystal of approximate dimensions 0.1 x 0.1 x 0.1 mm recrystallized, by cooling, from a 1,2-dichloroethane solution, showed no symmetry. A zero level Weissenberg also indicated the absence of 'right-left' symmetry and it was concluded that the crystal was triclinic. The photographs showed as well that the crystal had cracked.

Spots of considerably smaller intensity were found adjacent to the large ones. Two axes were chosen (close to 90° apart) and they were labeled b^* and c^*. The a^*b^* and a^*c^* zones were recorded on film using the precession camera and, from the spacings, the values $y_a = 3.26$, $y_b = 2.58$ and $y_c = 3.47$ mm were obtained. These correspond to reciprocal cell lengths of 0.0765^{526}, 0.0605^{050} and 0.081^{3295} Å^{-1} for a^*, b^* and c^* respectively. With measured reciprocal angles of $\alpha^* = 103.8^{\circ}$, $\beta^* = 69.3^{\circ}$ and $\gamma^* = 86.0^{\circ}$, the approximate real cell parameters were calculated[205] and used in alignment of the triclinic crystal on the diffractometer.

The (0,11,0) and the (0,0,7) reflections were found on the goniometer and centered. With the careful choice of a right-handed set of axes, the (8,0,0) reflection was predicted using the rough cell parameters and was located. An improved orientation matrix was obtained using the centered angles for these three reflections. A total of 12 reflections were centered at both plus and minus 2θ and the results were averaged. These were the (0,11,0), (0,-11,0), (9,1,0), (-9,-1,0), (9,0,-7), (-9,0,7), (2,0,6), (-2,0,-6), (3,-9,1), (-3,9,-1), (0,5,5) and (0,-5,-5) reflections. Two cycles of least squares refinement gave the following refined cell parameters: $a = 14.207 \pm 0.004$, $b = 17.321 \pm 0.005$, $c = 13.736 \pm 0.004$ Å, $\alpha = 73.63 \pm 0.02$, $\beta = 112.44 \pm 0.02$, $\gamma = 99.78 \pm 0.02^{\circ}$. The unit cell volume was calculated to be $2990.^{5}$ Å^3.

A reduced cell was calculated using the Delauney reduction.[206] The reduced cell is $a_r = 14.207$, $b_r = 17.321$, $c_r = 18.830$ Å, $\alpha_r = 135.64$, $\beta_r = 97.14$, $\gamma_r = 99.89^{\circ}$. These cell parameters are derived from the cell used in practice by the relationships: $\vec{a}_r = \vec{a}$, $\vec{b}_r = \vec{b}$, $\vec{c}_r = \vec{b} + \vec{c}$.

The crystal density was measured by flotation in zinc iodide aqueous solution. The observed density was 1.538 g cm^{-3}. Based on 2 molecules per unit cell, a volume of 2990.5 $Å^3$ and a formula weight of 1296.7 g $mole^{-1}$ for $Co_2As_4C_{66}H_{54}O_2$, the calculated density is 1.44 g cm^{-3}. If the 2 molecules of 1,2-dichloroethane are included, the calculated density becomes 1.55 g cm^{-3} which is in better agreement with the observed density.

Data collection was effected using those instrumental parameters described in Table IV-B-6. A total of 6047 reflections were measured of which 512 were absent and 1377 were less than 3σ. Thus 4158 reflections were used for structure solution and refinement. Absorption corrections were not applied since the crystal size was very small ($\mu = 30.30$ cm^{-1}).

The phase problem was solved by computing a Patterson map for the entire unit cell at 0.5Å resolution and reproducing it onto glass sheets to give a three-

TABLE IV-B-6

DATA COLLECTION PARAMETERS FOR

$Co_2(CO)_2(PhCCPh)(Ph_2AsCH_2AsPh_2)_2 \cdot ClH_2CCH_2Cl$

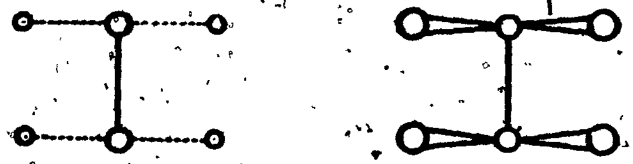
Radiation used:		Mo K_α (λ = 0.71069Å)	
Pulse height analyzer		100%	
Upper level		6.0	
Lower level		2.0	
Attenuators		Used	
Space group routine used:		None	
maximum *h*:	13	minimum *h*:	0
maximum *k*:	16	minimum *k*:	-16
maximum *l*:	13	minimum *l*:	-13
maximum 2θ:	40.0°	minimum 2θ:	4.0°
Standards used (*hkl*)		(8,0,0) (0,11,0) (0,0,6)	
Value and variation for scaling		13000 ± 15%	
Interval		every 50 reflections	
Background		40 second counts	
Base length of scan		2.0°	
Total number of reflections collected:		6047	

dimensional representation of the vector density. The pattern of peaks on the Patterson map was identified as being due to the vectors between the atoms of the arsenic-cobalt framework described in Figure IV-B-1. A peak (marked with an asterisk) with unitary multiplicity was chosen as arsenic atom 1. The peak was labeled u_1, v_1, w_1. The atom As1 was thus located at x_1, y_1, z_1 ($u_1/2, v_1/2, w_1/2$) in the real cell. The remaining five Patterson inter-heavy atom vectors were labeled and their u, v, w co-ordinates were recorded. These were referred to the real cell origin by subtracting the As1 cell co-ordinates (x_1, y_1, z_1). This procedure is shown in Table IV-B-7.

The co-ordinates listed in Table IV-B-7 were used in a structure factor calculation which gave a discrepancy index of 42.8%. One cycle of full matrix least squares isotropic refinement showed the atoms to be well-behaved and the discrepancy index dropped to 30.2%. An observed Fourier was now calculated at one-third angström resolution and it revealed all remaining non-hydrogen atoms in the complex as well as a molecule of 1,2-dichloroethane. The positions of all these atoms were recorded, the distances and angles around them were computed to insure that no mistake was made in reading the co-ordinates, and a least squares refinement was undertaken.

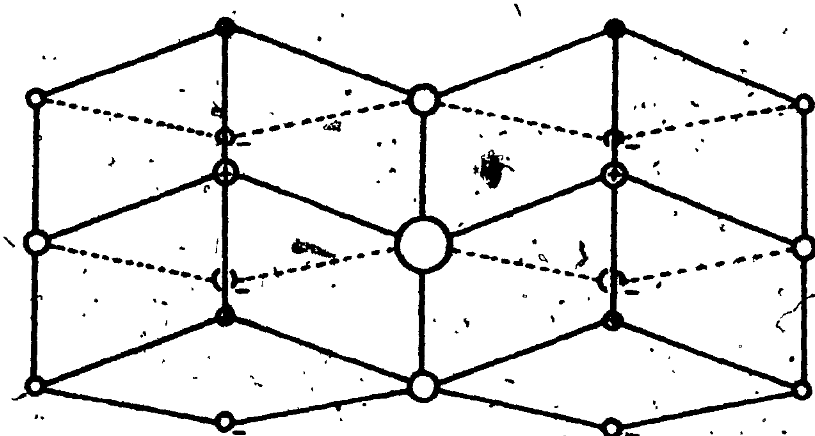
The atoms were separated into seven matrices

Figure IV-B-1. Patterson peaks for the vectors between heavy atoms in $Co_2(CO)_2(PhCCPh)(Ph_2AsCH_2AsPh_2)_2 \cdot ClH_2CCH_2Cl$.

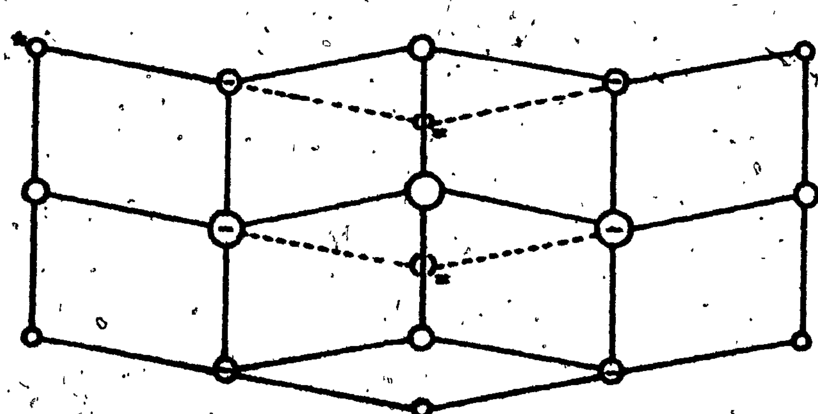


1 2

The two molecular heavy atom frameworks



Patterson peaks for intra-cluster vectors



Patterson peaks for inter-cluster vectors

TABLE IV-B-7

CALCULATION OF THE SIX HEAVY ATOM CO-ORDINATES (X,Y,Z) FROM PATTERSON CO-ORDINATES (U,V,W) IN $Co_2(CO)_2(PhCCPh)(Ph_2AsCH_2AsPh_2)_2 \cdot ClH_2CCH_2Cl$

ATOM NAME	(u,v,w)	− (x_1,y_1,z_1)	= (x,y,z)
As1	0.600	0.300	0.300
	0.756	0.378	0.378
	0.614	0.307	0.307
As2	0.730	0.300	0.430
	0.550	0.378	0.172
	0.788	0.307	0.481
As3	0.384	0.300	0.084
	0.660	0.378	0.282
	0.524	0.307	0.217
As4	0.520	0.300	0.220
	0.470	0.378	0.092
	0.664	0.307	0.357
Co1	0.610	0.300	0.310
	0.650	0.378	0.272
	0.770	0.307	0.463
Co2	0.430	0.300	0.130
	0.564	0.378	0.186
	0.680	0.307	0.373

in somewhat random fashion. There was at least one heavy atom per matrix however and the isotropic temperature factors were all started at 3.5. The structure factor calculation preceeding the refinement gave a discrepancy factor of 25.6% whereas, following one cycle of isotropic refinement, the R factor was 14.4%. Most of the atoms seemed well-behaved although the solvent molecule gave rather large isotropic temperature factors which further increased in the second isotropic refinement cycle. The atoms were shuffled around between the seven matrices to ensure a certain degree of co-relation between them. The R factor was now 12.7% whereas the weighted R factor was 12.2%.

The ten phenyl rings of the complex were converted to rigid groups and this reduced the number of ring parameters from 24 to 12 for each ring. The program *NUCLS4* was then used to further refine the structure. One cycle afforded isotropic convergence at 10.3% (weighted R factor of 9.4%). This refinement involved 199 parameters and 4158 reflections. Anomalous dispersion corrections were applied to both arsenic ($\Delta f' = 0.1$, $\Delta f'' = 2.2$) and cobalt ($\Delta f' = 0.4$, $\Delta f'' = 1.1$). All atoms but the rigid rings were allowed to refine anisotropically. Convergence occurred rapidly (in 2 cycles) to a final residual index of 8.6% and a final weighted index of 7.5%. The "goodness-of-fit" parameter was 3.04 for 4158 reflections. The final parameter shifts were, on the average, only 10% of their estimated standard deviations. Attempts were not made to locate the 54 hydrogen atoms on the final difference Fourier map (maximum peak = 1.0 $\Delta e\text{Å}^{-3}$) since it was impossible to include them in a structure factor calculation because of program restrictions. Their positions were calculated however (C-H distance of 0.98Å) and were used in assessing intermolecular contacts. The positions of ring carbon atoms were derived from the ring centers and orientations. The C-C bond length was taken as 1.390 Å and all angles as 120°. The isotropic thermal parameters were as refined by *NUCLS4* and both positional and thermal parameters can be found in Appendix C. Also found in Appendix C will be a list of the observed and calculated structure factors as well as the equations of the ten rigid ring planes of the structure.

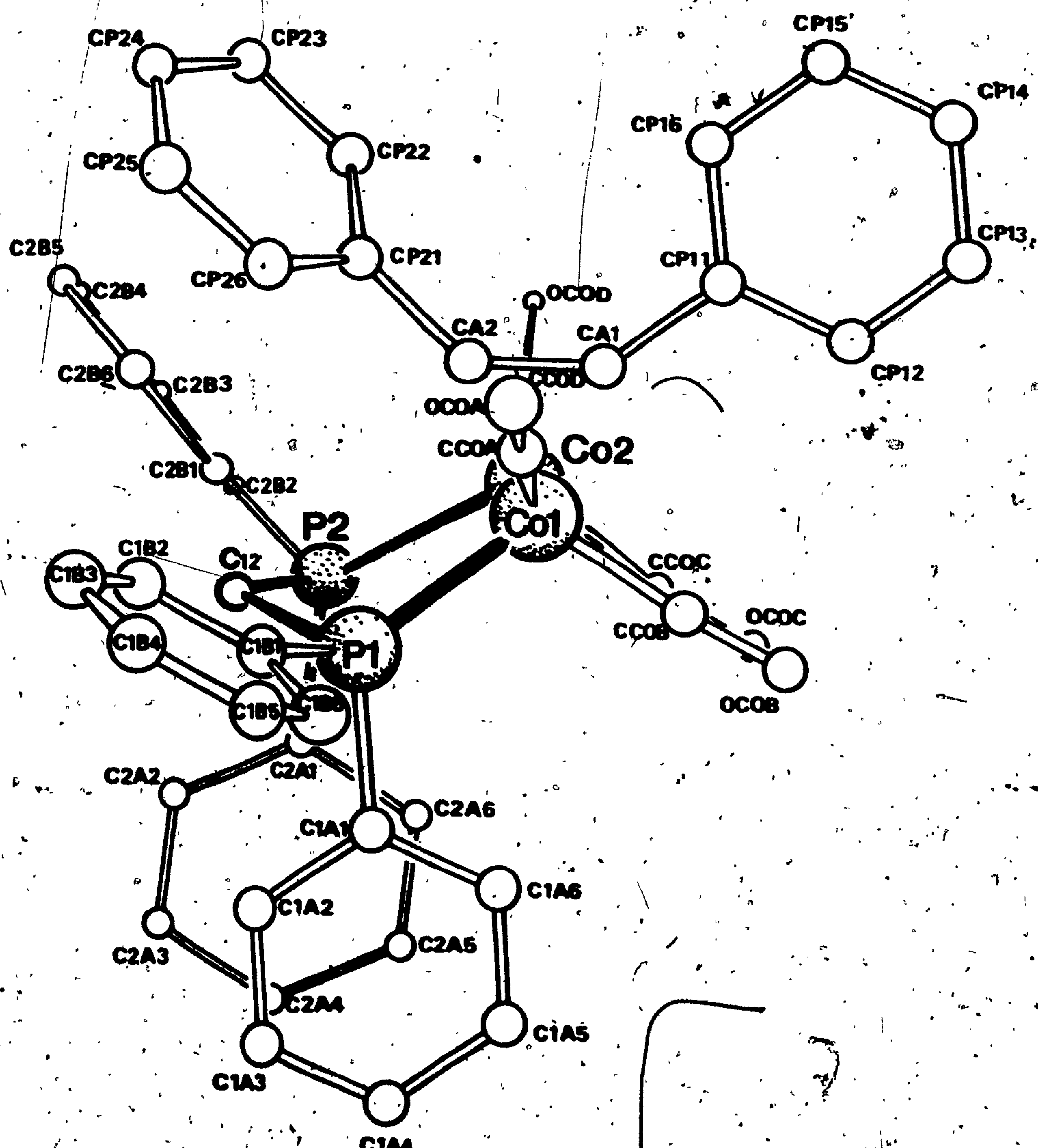
SECTION C. RESULTS AND DISCUSSION

The molecules studied by X-ray crystallography and reported in this section possess no features which, taken by themselves, are novel. Diphenylacetylenic complexes have been extensively studied as well as various complexes with bidentate bridging ligands (see Section A). The combination of these features in one molecule, however, is unique. Features of the various bonded species must be compromised in order for the molecules to form. This is especially true for the di-μ-{bis(diphenylarsino)methane}-μ-(diphenylacetylene)dicarbonyldicobalt · 1,2-dichloroethane solvate which must accommodate the steric interactions of ten phenyl groups.

1. The Crystal and Molecular Structure of μ-{bis(diphenylphosphino)methane}-μ-(diphenylacetylene)tetracarbonyldicobalt(0).

The molecule $Co_2(CO)_4(PhCCPh)(Ph_2PCH_2PPh_2)$ consists of a dicobalt framework to which is bonded a diphenylacetylene molecule, a bis(diphenylphosphino)methane ligand bridging the two cobalt atoms, and four terminal carbonyls, two on each cobalt atom. The molecule is illustrated in Figure IV-C-1 which also describes the

Figure IV-C-1. The molecular configuration and numbering scheme for μ-{bis(diphenylphosphino)methane}-μ-(diphenylacetylene)tetracarbonyldicobalt.


CP24
CP23
CP15'
CP14
CP16
CP22
CP25
CP13
CP11
CP21
C2B5
CP26
OCOD
C2B4
CA2
CA1
CP12
C2B6
C2B3
CCOD
OCOA
CCOA
Co2
C2B1
C2B2
P2
Co1
C1B2
C12
C1B3
CCOC
C1B4
C1B1
P1
CCOB
OCOC
C1B5
C1B6
OCOB
C2A2
C2A1
C2A6
C1A1
C1A6
C1A2
C2A3
C2A5
C2A4
C1A5
C1A3
C1A4

numbering scheme for the various atoms in the molecule.

It can be seen that the five-membered ring (Co1-Co2-P2-C12-P1) is not planar but that the methylene carbon atom is bent up toward the diphenylacetylene ligand. This may be the result of possible interactions with the adjacent carbonyl ligands or an artifact of the ligand itself. The angle between the plane P1-C12-P2 and the least squares plane to the atoms Co1-Co2-P2-P1 is 135.4°.

Figure IV-C-2 gives a view down the Co1-Co2 vector of this molecule but in a direction opposite to that used in Figure IV-C-1. It will be seen from this projection that the Co1-Co2 vector is not parallel to the P1-P2 vector. The angle between these vectors is 7.4°. The twist of the bent bidentate bridging ligand is such that one of the phenyl groups attached to this bidentate ligand may well determine the direction of bend of the acetylenic phenyl group.

The bond lengths and angles for the complex are quoted in Tables IV-C-1 and IV-C-2. The cobalt-cobalt distance of 2.459(2)Å is compatible with values measured for acetylenic dicobalthexacarbonyl systems. There are two pairs of carbonyl ligands, the first (CCOA,CCOD) displaying a Co-C distance 0.06[5]Å smaller that the other (CCOB,CCOC). CCOA

Figure IV-C-2: A view of μ-{bis(diphenylphosphino)methane}-μ-(diphenylacetylene)tetracarbonyldicobalt down the Co–Co bond vector.

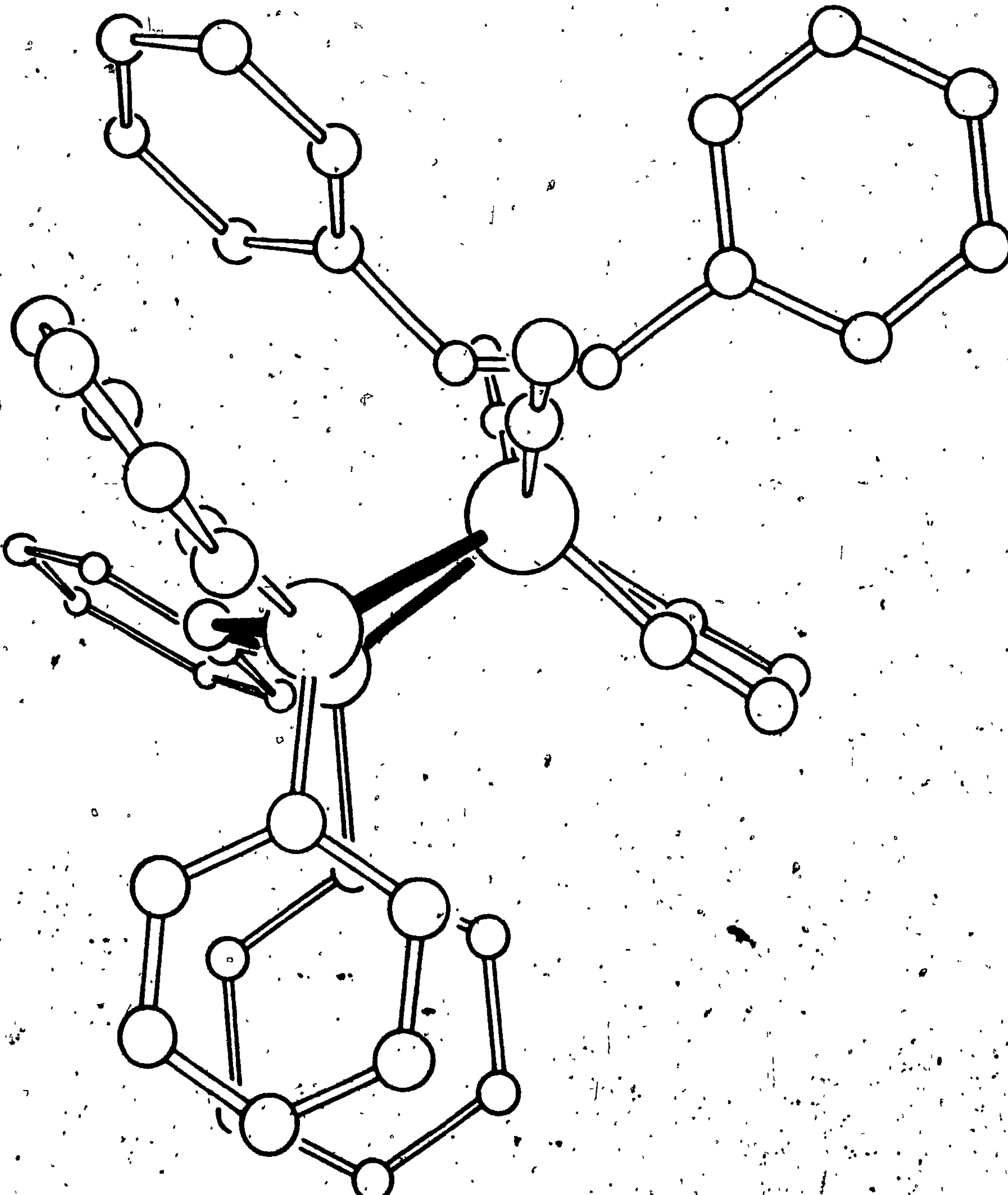


TABLE IV-C-1

BOND LENGTHS (Å) IN μ-{BIS(DIPHENYLPHOSPHINO)METHANE}-μ-(DIPHENYLACETYLENE)TETRACARBONYLDICOBALT(0).

Co1 -Co2 :	2.459(2)	CA1 -CA2 :	1.33(1)
Co1 -CCOA:	1.70(1)	Co2 -CCOD:	1.71(1)
Co1 -CCOB:	1.78(1)	Co2 -CCOC:	1.76(1)
Co1 -CA1 :	1.97(1)	Co2 -CA2 :	1.94(1)
Co1 -CA2 :	1.95(1)	Co2 -CA1 :	1.92(1)
CCOA-OCOA:	1.16(2)	CCOC-OCOC:	1.13(2)
CCOB-OCOB:	1.14(2)	CCOD-OCOD:	1.14(2)
Co1 -P1 :	2.210(3)	Co2 -P2 :	2.215(3)
P1 -P2 :	2.946(4)		
P1 -C12 :	1.84(1)	P2 -C12 :	1.84(1)
P1 -C1A1:	1.822(7)	P2 -C2A1:	1.809(7)
P1 -C1B1:	1.822(7)	P2 -C2B1:	1.829(7)
CA1 -CP11:	1.46(1)	CA2 -CP21:	1.49(1)

TABLE IV-C-2

BOND ANGLES (°) IN μ-{BIS(DIPHENYLPHOSPHINO)METHANE}-μ-(DIPHENYLACETYLENE)TETRACARBONYLDICOBALT(0).

P1 -Co1 -Co2 :	93.2(1)	P2 -Co2 -Co1 :	98.8(1)
P1 -Co1 -CCOB:	109.2(4)	P2 -Co2 -CCOC:	111.8(5)
P1 -Co1 -CCOA:	98.5(4)	P2 -Co2 -CCOD:	97.8(5)
P1 -Co1 -CA2 :	101.7(3)	P2 -Co2 -CA2 :	97.5(3)
CA1 -Co1 -Co2 :	50.0(3)	CA1 -Co2 -Co1 :	51.6(3)
CA1 -Co1 -CCOB:	101.4(5)	CA1 -Co2 -CCOC:	103.8(6)
CA1 -Co1 -CCOA:	105.0(5)	CA1 -Co2 -CCOD:	100.0(6)
CA1 -Co1 -Co2 :	39.7(4)	CA1 -Co2 -CA2 :	40.2(4)
Co2 -Co1 -CCOB:	102.2(4)	Co1 -Co2 -CCOC:	97.8(5)
CCOB-Co1 -CCOA:	101.0(5)	CCOC-Co2 -CCOD:	99.1(6)
CCOA-Co1 -CA2 :	98.5(5)	CCOD-Co2 -CA2 :	102.0(5)
CA2 -Co1 -Co2 :	50.7(3)	CA2 -Co2 -Co1 :	50.8(3)
Co2 -Co1 -CCOA:	148.8(4)	Co1 -Co2 -CCOD:	149.8(4)
Co1 -P1 -C12 :	109.7(3)	Co2 -P2 -C12 :	108.9(3)
Co1 -P1 -C1A1:	121.8(3)	Co2 -P2 -C2A1:	123.8(3)
Co1 -P1 -C1B1:	115.4(3)	Co2 -P2 -C2B1:	111.9(3)
C12 -P1 -C1A1:	103.4(4)	C12 -P2 -C2A1:	103.5(4)
C12 -P1 -C1B1:	103.2(4)	C12 -P2 -C2B1:	104.3(4)
C1A1-P1 -C1B1:	101.3(4)	C2A1-P2 -C2B1:	102.6(4)
P1 -C12 -P2 :	106.4(5)		
CP11-CA1 -CA2 :	143.2(9)	CP21-CA2 -CA1 :	137.7(9)
CP11-CA1 -Co1 :	133.8(7)	CP21-CA2 -Co1 :	136.9(7)
CP11-CA1 -Co2 :	133.5(7)	CP21-CA2 -Co2 :	135.2(7)
CA2 -CA1 -Co1 :	69.4(6)	CA1 -CA2 -Co1 :	70.9(6)
CA2 -CA1 -Co2 :	70.7(6)	CA1 -CA2 -Co2 :	69.1(6)
Co1 -CA1 -Co2 :	78.5(4)	Co1 -CA2 -Co2 :	78.5(4)
Co1 -CCOA-OCOA:	179(1)	Co2 -CCOD-OCOD:	176(1)
Co1 -CCOB-OCOB:	175(1)	Co2 -CCOC-OCOC:	173(1)

and CCOD are *trans* to the cobalt–cobalt bond whereas the longer Co–C carbonyls are *trans* to the acetylene ligand. This confirms the *trans* influence also found in tris(hexacarbonyldicobalt-π-ethynyl)arsine.

There appears to be very little difference between the average Co–P length of 2.213Å and the sum of covalent radii which gives a value of 2.232Å.[132] There is perhaps some double bond character but it is minimal. The P–P distance is 2.946(4)Å for the bridging ligand. Equivalent distances in the planar chelate complexes are 2.792Å[185] and 2.766Å.[136] The angle in $Co_2(CO)_4$·(PhCCPh)($Ph_2PCH_2PPh_2$) is 106.4° whereas the P–C–P angles in the planar chelate complexes average 96.0°. The Co–P–C angles are about 15° larger than the equivalent angles in these complexes.

Bond lengths and angles observed for the diphenylacetylene ligand are in very good agreement with those observed in other such complexes. There appears to be little change in the acetylene due to the presence of the bulky bidentate ligand. The degree of twist of the phenyl rings with respect to the CP11–CA1–CA2–CP21 plane† totals 53.6°, a value similar to that observed for μ-diphenylacetylenehexacarbonyldicobalt[77] (62°), bis(cyclopentadienyl)-μ-diphenylacetylenedinickel (60°)[194] and W(O)π-(C_5H_5)σ-(C_5H_6)(PhCCPh) (57°).[195] In the $Co_2(CO)_4$(PhCCPh)·

†Sum of angles between two phenyl ring planes and plane quoted.

($Ph_2PCH_2PPh_2$) molecule, the diphenylacetylene phenyl ring above the carbonyl ligands (CCOB/CCOC) is aligned such that its plane approximately bisects the distance between the two carbonyls. The other phenyl ring appears to be perturbed by the phenyl groups attached to the phosphorus atoms.

The diphenylacetylene ligand is not linear but there are angles of 137.7° for CP21-CA2-CA1 and 143.2° for CP11-CA1-CA2. The CA1-CA2 distance is 1.33(1)Å which indicates that the best approximation for the bond is double rather than triple. Since the phenyl carbon is considered sp^2 hybridized, the CP11-CA1 and CP21-CA2 distances should reflect two sp^2 hybridized carbons bonded together. The value for this is 1.476Å [192] which compares favourably with the measured distances of 1.46 and 1.49Å. The C_{sp^2}-C_{sp} distance is estimated as 1.426Å. In the free ligand, studied by X-ray crystallography in 1938, [207] the C≡C distance was 1.19Å, the acetylenic carbon-phenyl carbon distance 1.40Å and the average phenyl bond 1.39Å. The acetylene was linear.

Again with this compound, the angle between the acetylenic carbons vector and the cobalt-cobalt vector is very close to a right angle (91.3°). There is a slight twist (7.7°) of the CCOA-Co1-Co2-CCOD plane with respect to the CA1-CA2 vector. The CCOA-Co1-Co2 and CCOD-Co2-Co1 angles are 148.8 and 149.9° respectively which are similar to those angles found for tris(hexacarbonyldicobalt-π-ethynyl)arsine. In summation, the bonding of the diphenylacetylene unit seems quite usual.

The atoms which are not part of the phenyl rings were refined anisotropically. These atoms do not appear to be very anisotropic. The major, median and minor axes of the thermal ellipsoids are listed in Table IV-C-3 along with their direction cosines for the individual atoms.

As expected, non-bonded intramolecular contacts below 3.0Å are plentiful and they are all quoted in Table IV-C-4. Although some of these are close to the sum of van der Waal's radii, this is but indicative of the degree of steric strain associated with the molecule. Intermolecular contacts to 3.0Å are quoted in Table IV-C-5. No untoward values are found here. Figure IV-C-3 gives the packing diagram of the molecules in the monoclinic cell as viewed down the *a* axis.

2. The Crystal and Molecular Structure of the Di-μ-{bis(diphenylarsino)methane}-μ-(diphenylacetylene)dicarbonyldicobalt · 1,2-Dichloroethane Solvate.

The molecules are similar to those of μ-{bis(diphenylphosphino)methane}-μ-(diphenylacetylene)tetra-

TABLE IV-C-3

THERMAL VIBRATION ELLIPSOIDS[a] - μ-{BIS(DIPHENYLPHOSPHINO)-METHANE}-μ-(DIPHENYLACETYLENE)TETRACARBONYLDICOBALT

Atom	Axes[b]	Direction Cosines		
Co1	4.60	0.63355	0.08459	-.76907
	3.29	0.53749	0.66683	0.51615
	2.70	0.55645	-.74040	0.37700
Co2	4.83	0.76129	0.55741	-.33134
	3.95	0.40148	-.80638	-.43429
	2.94	0.50925	-.19760	0.83762
P1	3.98	0.78170	0.37154	-.50093
	2.88	0.62284	-.42422	0.85732
	2.70	-.03176	0.82583	0.56303
P2	4.42	0.69460	0.53972	-.47568
	3.22	0.67693	-.26646	0.68611
	2.62	0.23460	-.79856	-.55044
C12	5.09	0.92405	0.37214	0.08770
	3.51	-.06681	-.06870	0.99540
	1.65	0.37651	-.93563	-.03862
CA1	5.17	0.43885	-.53332	-.72319
	3.48	0.39683	-.60704	0.68848
	2.46	0.00622	0.58913	0.05473
CA2	4.89	0.81433	-.00777	-.58035
	3.31	0.17830	0.95488	0.23749
	2.33	0.55230	-.29691	0.77897
CCOA	5.35	0.79189	-.55598	-.25268
	4.63	0.31262	0.01360	0.94978
	3.03	0.52468	0.83108	-.18558
OCOA	8.27	0.51386	0.33926	0.78793
	7.66	0.16468	0.86241	-.47869
	4.07	0.84194	-.37570	-.38732
CCOB	6.92	0.40613	-.15047	-.90135
	4.73	0.41990	0.90681	0.03779
	2.27	0.81164	-.39378	0.43144
OCOB	11.40	0.19720	-.26295	-.94444
	6.48	0.96942	0.19575	0.14791
	3.18	0.14593	-.95574	0.29351

TABLE IV-C-3 (CONT'D)

CCOC	8.19	0.22711	-.84358	-.48664
	6.69	0.96897	0.24588	0.02588
	3.86	0.09779	-.47741	0.87322
OCOC	17.78	0.11813	-.74352	-.65821
	9.53	0.96354	-.07447	0.25699
	4.65	0.24013	0.66455	-.70762
CCOD	9.16	0.70630	0.51933	-.48112
	5.74	0.59695	-.80225	0.01027
	3.32	0.38062	0.29444	0.87659
OCOD	16.08	0.58891	0.64345	-.48909
	11.64	0.79176	-.58069	0.18937
	3.95	0.16213	0.49877	0.85143

a Given in the order of major, median and minor axes.

b Axes lengths are in units of B where the root mean square displacement $(\overline{U}^2)^{\frac{1}{2}} = (B/8\pi^2)^{\frac{1}{2}}$.

TABLE IV-C-4

NON-BONDED INTRAMOLECULAR CONTACTS (Å) FOR μ-{BIS(DIPHENYLPHOSPHINO)METHANE}-μ-(DIPHENYLACETYLENE)TETRACARBONYLDICOBALT

P1 -CCOA:	2 983	P2 -CCOD:	2.980
P1 -H121:	2.324	P2 -H121:	2.331
P1 -H122:	2.324	P2 -H122:	2.331
C12 -C1A1:	2.870	C12 -C2A1:	2.868
C12 -C1B1:	2.867	C12 -C2B1:	2.899
C12 -H1A2:	2.976	C12 -H2B6:	2.760
C12 -H1B2:	2.608		
CA1 -CP21:	2.632	CA2 -CP11:	2.645
CA1 -CCOA:	2.916	CA1 -CCOD:	2.789
CA1 -CCOB:	2.901	CA1 -CCOC:	2.899
CA2 -CCOA:	2.770	CA2 -CCOD:	2.846
CA2 -H122:	2.995	CCOA-HP26:	2.768
CCOA-CCOB:	2.689	CCOC-CCOD:	2.646
CCOB-H1A6:	2.508	CCOC-H2A6:	2.562
OCOB-H1A6:	2.732	OCOC-H2A6:	2.809
CCOB-HP12:	2.802	CCOD-HP22:	2.787
OCOB-HP12:	2.817	OCOD-HP22:	2.938
C1A1-C1B1:	2.818	C1A1-H1B6:	2.986
C1A1-H121:	2.835	C1A2-H121:	2.786
C1B1-H1A2:	2.941	C1B1-H122:	2.977
C1B2-HP26:	2.918	C1B2-H122:	2.861

TABLE IV-C-4 (CONT'D)

C2A1-C2B1:	2.839	C2A1-H2B2:	2.769
C2A1-H121:	2.774	C2A2-H121:	2.808
C2B1-H2A2:	2.947	C2B1-H122:	2.911
C2B6-H122:	2.784		
CP21-H2B6:	2.943	CP21-HP16:	2.999
CP21-H122:	2.913	CP22-HP16:	2.831
CP26-H122:	2.735		
H1A2-H121:	2.334	H1B2-HP26:	2.668
H1B2-H121:	2.640	H1B2-H122:	2.198
H2A2-H121:	2.477	H2B6-H122:	2.119
HP16-HP22:	2.584	HP26-H122:	2.585

TABLE IV-C-5

INTERMOLECULAR CONTACTS (Å) FOR μ-{BIS(DIPHENYLPHOSPHINO)-METHANE}-μ-(DIPHENYLACETYLENE)TETRACARBONYLDICOBALT.[a,b]

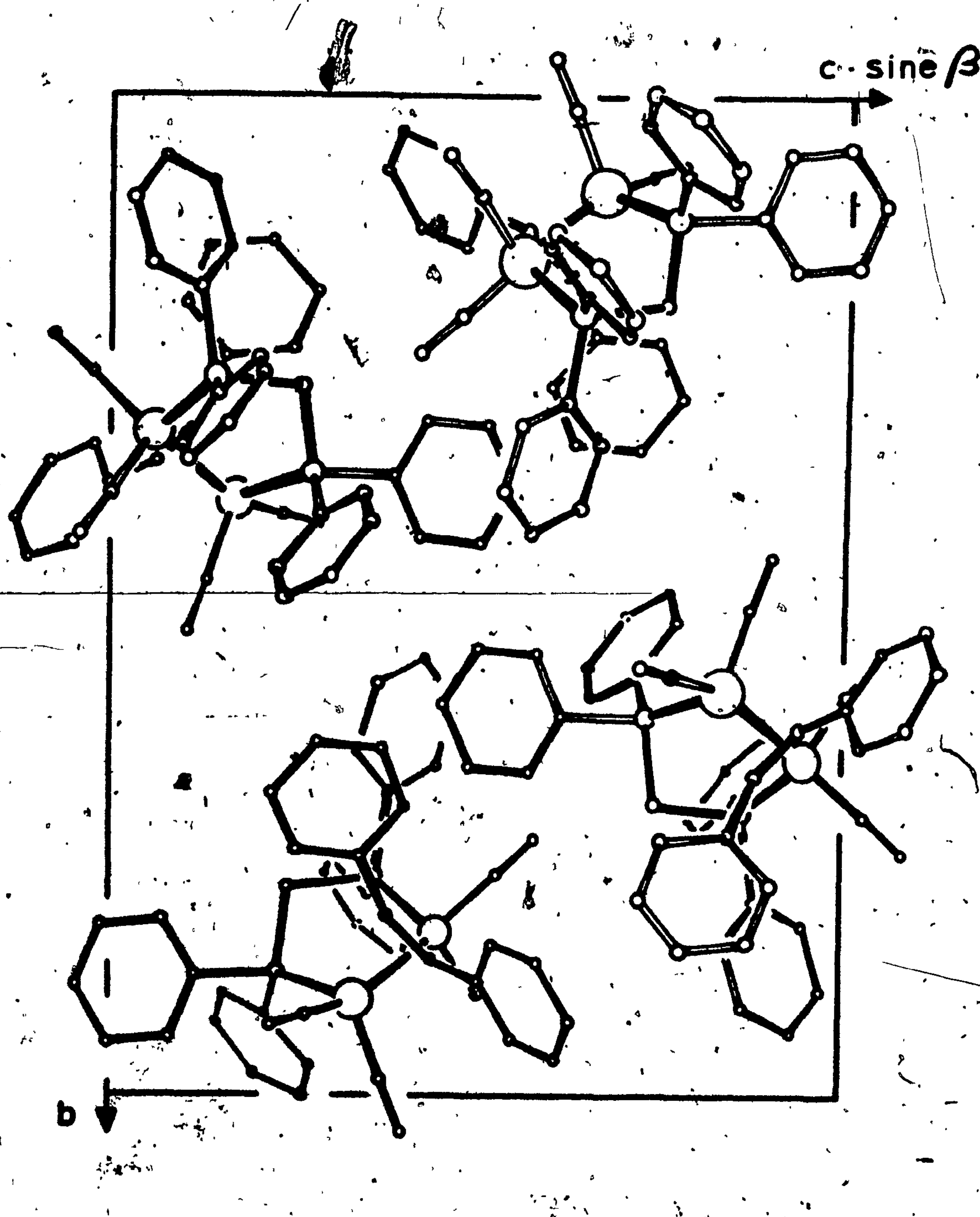
C1A3-H1B5:	2.901	V	H1A2-HP22:	2.843	VI
C2A3-H1B3:	2.885	VII	H1A4-HP13:	2.880	IV
C2B3-H2B4:	2.835	II	H1A5-HP12:	2.950	IV
C2B4-H2B4:	2.877	II	H1A6-HP24:	2.922	VIII
C2B5-HP14:	2.962	VI	H1B2-HP15:	2.479	VI
CCOB-HP14:	2.987	II	H1B2-HP16:	2.805	VI
OCOB-HP14:	2.891	II	H1B6-HP23:	2.794	VIII
OCOA-HP13:	2.977	II	H2A4-HP16:	2.646	I
OCOA-H2B5:	2.779	VIII	H2A5-HP15:	2.974	I
OCOB-HP24:	2.947	VIII	H2A5-HP12:	2.668	IV
OCOC-H1A5:	2.793	IV	H2A5-HP13:	2.695	IV
OCOC-H1A6:	2.695	IV	H2B2-H1B3:	2.811	VII
H1A2-OCOD:	2.970	VI	H2B3-H2B4:	2.212	II
H2A3-OCOD:	2.903	VI	H2B4-H2B4:	2.303	II
H2A5-CP15:	2.990	I	H2B5-HP14:	2.408	VI
			H2B6-HP14:	2.838	VI

[a] Only atomic contacts less than 3.0Å are quoted.

[b] The following transformations give the position of the second atom listed relative to the first which has the co-ordinates (x, y, z) listed in Table B-2, Appendix B:

I	$1 + x, y, z$	V	$1 - x, -y, 1 - z$
II	$1 - x, -y, -z$	VI	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
III	$-x, 1 - y, -z$	VII	$\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$
IV	$1 - x, 1 - y, -z$	VIII	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$

Figure IV-C-3. Packing diagram for molecules of $Co_2(CO)_4 \cdot$ $(PhCCPh)(Ph_2PCH_2PPh_2)$ in the monoclinic cell as viewed down the *a* axis.


c · sine β
b

carbonyldicobalt. The two carbonyl ligands *trans* to the CA2 atom in this complex are replaced with a second bis(diphenylarsino)methane ligand in $Co_2(CO)_2(PhCCPh)\cdot(Ph_2AsCH_2AsPh_2)_2$. Figure IV-C-4 provides a view of the molecule with all the atoms included. The cobalt-arsenic-methylene carbon skeleton is accentuated by shadowing and darkening of the bonds. The numbering scheme is also given in this diagram.

The As2-As4 bridging ligand has a configuration similar to that of the diphosphine in the $Co_2(CO)_4(PhCCPh)(Ph_2PCH_2PPh_2)$ complex with the methylene carbon (C24) pointing 'upwards' towards the diphenylacetylene moiety. The angle between the As2-C24-As4 plane and the least squares plane to Co1-Co2-As2-As4 is 152.3° which is approximately 17° larger than that in $Co_2(CO)_4(PhCCPh)(Ph_2PCH_2PPh_2)$. The angle of twist of the ligand (angle between the Co1-Co2 vector and the As2-As4 vector) is 7.9° which is very similar to that found in the 1:1 phosphorus complex.

The second bidentate bridge is bent <u>away</u> from the diphenylacetylene ligand by approximately the same angle (151.1°) although the ligand is not twisted as can clearly be seen from Figure IV-C-5. The Co1-Co2 vector and the As1-As3 vector are parallel for all intents and purposes.

Figure IV-C-4. The molecular configuration and numbering scheme for di-μ-{bis(diphenylarsino)methane}-μ-(diphenylacetylene)dicarbonyldicobalt.

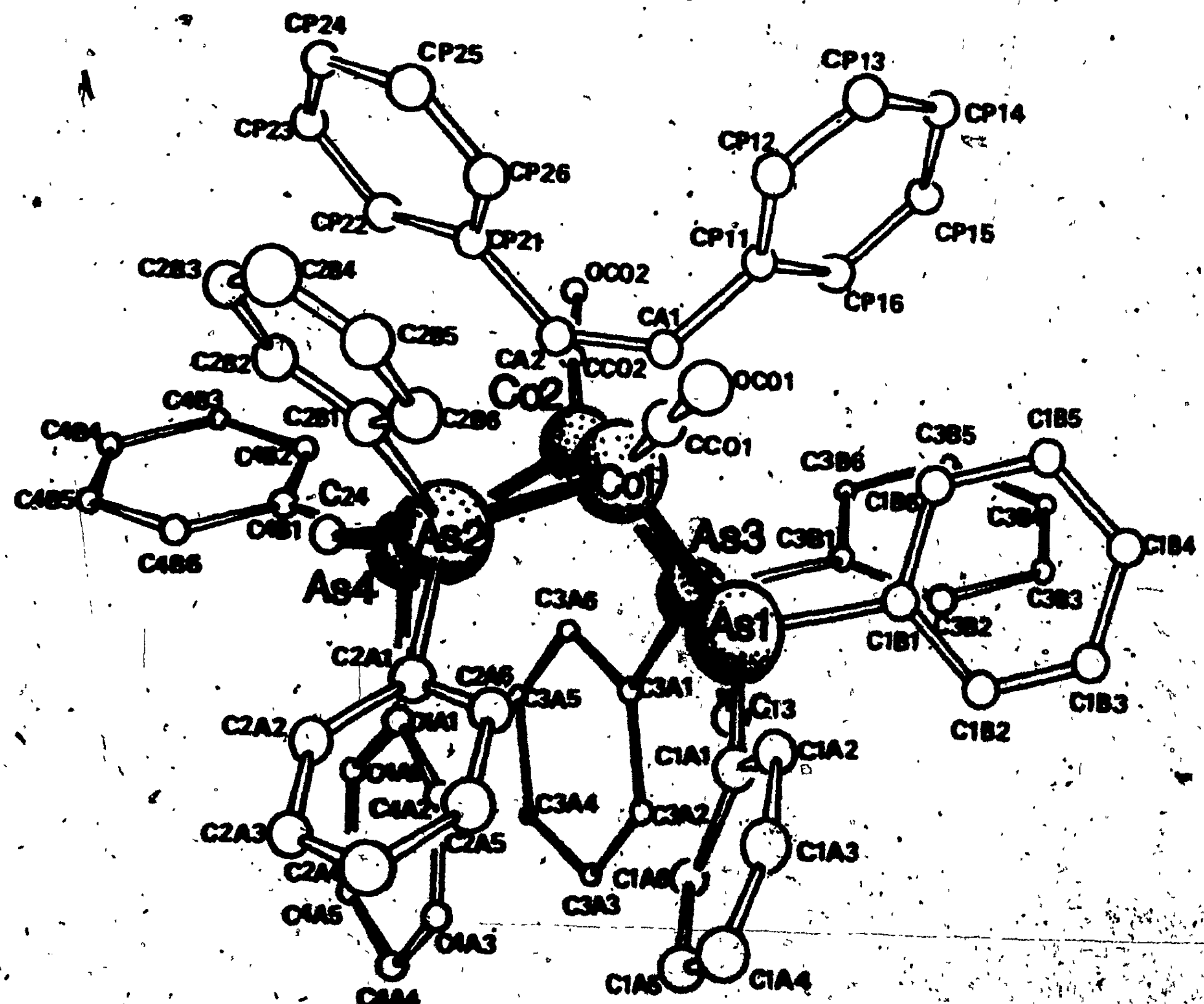
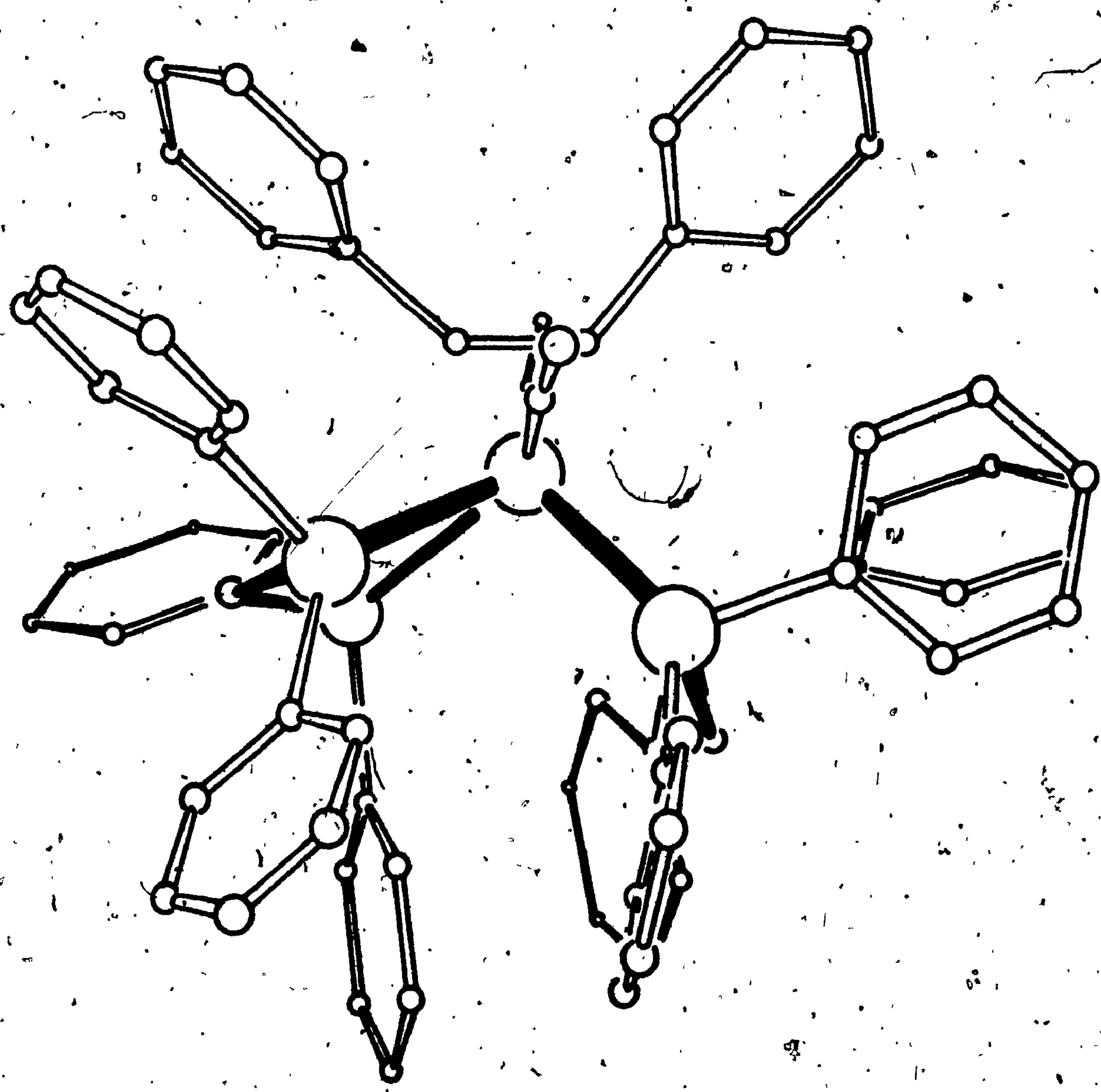

CP24
CP25
CP23
CP26
CP22
CP21
CP13
CP14
CP12
CP11
CP15
CP16
C2B3
C2B4
C2B5
C2B2
OC02
CA1
CA2
CC02
OC01
Co2
CC01
Co1
C2B1
C2B6
C4B4
C4B3
C4B2
C4B5
C4B1
C24
As2
As3
As4
As1
C4B6
C3B5
C1B5
C3B6
C1B6
C3B1
C1B4
C3B3
C3B2
C1B1
C1B3
C1B2
C3A6
C2A1
C2A6
C3A5
C3A1
C13
C2A2
C1A1
C1A2
C3A4
C3A2
C2A3
C2A5
C1A3
C1A6
C3A3
C4A5
C4A3
C4A4
C1A5
C1A4

Figure IV-C-5. A view of di-μ-{bis(diphenylarsino)methane}-μ-(diphenylacetylene)dicarbonyldicobalt down the Co-Co bond vector.



Tables IV-C-6 and IV-C-7 give the bond lengths and angles respectively for the di-μ-{bis(diphenylarsino)methane}-μ-(diphenylacetylene)dicarbonyldicobalt 1,2-dichloroethane solvate. The cobalt-arsenic distances average 2.334Å which, as with the phosphorus 1:1 complex, is near the sum of covalent radii for the cobalt and arsenic atoms. The cobalt-cobalt bond is 2.518(4)Å which is significantly longer than that in $Co_2(CO)_4(PhCCPh)(Ph_2PCH_2PPh_2)$ (2.459(2)Å). In point of fact, the value of 2.518Å is at the upper limit of the range of cobalt-cobalt bond lengths reported.[208] An explanation for this 0.06Å difference in cobalt-cobalt distances for the two complexes may well depend upon the difference in the 'bites' of the two ligands. The average As-As distance in the complex is 3.202Å whereas the P-P distance in $Co_2(CO)_4(PhCCPh)(Ph_2PCH_2PPh_2)$ is 2.946Å. The Co-As-C(methylene) angles average 113.4° whereas the Co-P-C(methylene) angles average only 109.3°. Both these facts imply that the bridging bidentate arsenic ligand may be causing the Co-Co bond to stretch to accommodate the ligands.

While it is true that the 'bite' of the $(CH_3)_2As\overline{C{=}C(As(CH_3)_2)CF_2CF_2}$ ligand is even larger at 4.064Å in the complex $Co_2(CO)_6((CH_3)_2As\overline{C{=}C(As(CH_3)_2)CF_2CF_2})$,[172,173] the cobalt-cobalt bond is not appreciably stretched (2.483(4)Å) as in the complex reported here. It must be remembered that two of the six carbonyls are bridging in the complex and this may contribute to the shortening of an otherwise

TABLE IV-C-6

BOND LENGTHS (Å) IN THE DI-μ-{BIS(DIPHENYLARSINO)METHANE}-μ-(DIPHENYLACETYLENE)DICARBONYLDICOBALT • 1,2-DICHLOROETHANE

Co1 -Co2 :	2.518(4)	CA1 -CA2 :	1.37(3)
Co1 -CCO1:	1.71(2)	Co2 -CCO2:	1.78(2)
Co1 -CA1 :	1.96(2)	Co2 -CA2 :	1.97(2)
Co1 -CA2 :	1.96(2)	Co2 -CA1 :	1.93(2)
CCO1-OCO1:	1.17(2)	CCO2-OCO2:	1.13(2)
Co1 -As1 :	2.326(4)	Co2 -As3 :	2.332(4)
Co1 -As2 :	2.330(3)	Co2 -As4 :	2.348(3)
As1••As3 :	3.165(3)	As2••As4 :	3.240(3)
As1 -C13 :	2.01(2)	As3 -C13 :	1.99(2)
As1 -C1A1:	1.96(1)	As3 -C3A1:	1.95(1)
As1 -C1B1:	1.98(1)	As3 -C3B1:	1.99(1)
As2 -C24 :	1.98(2)	As4 -C24 :	2.01(2)
As2 -C2A1:	1.97(1)	As4 -C4A1:	1.95(1)
As2 -C2B1:	1.98(1)	As4 -C4B1:	1.95(1)
CA1 -CP11:	1.48(2)	CA2 -CP21:	1.50(2)
CS1 -Cl1 :	1.79(3)	CS2 -Cl2 :	1.82(4)
CS1 -CS2 :	1.44(6)		

TABLE IV-C-7

BOND ANGLES (°) IN THE DI-μ-{BIS(DIPHENYLARSINO)METHANE}-μ-(DIPHENYLACETYLENE)DICARBONYLDICOBALT · 1,2-DICHLOROETHANE

As1 -Co1 -Co2 :	96.2(1)	As3 -Co2 -Co1 :	99.7(1)
As1 -Co1 -As2 :	110.0(1)	As3 -Co2 -As4 :	98.7(1)
As1 -Co1 -CCO1:	98.2(6)	As3 -Co2 -CCO2:	97.7(6)
As1 -Co1 -CA1 :	108.4(6)	As3 -Co2 -CA1 :	108.3(6)
CA2 -Co1 -Co2 :	50.3(6)	CA2 -Co2 -Co1 :	49.8(6)
CA2 -Co1 -As2 :	92.1(6)	CA2 -Co2 -As4 :	101.7(6)
CA2 -Co1 -CCO1:	107.9(9)	CA2 -Co2 -CCO2:	104.8(8)
CA2 -Co1 -CA1 :	41.0(8)	CA2 -Co2 -CA1 :	41.1(9)
Co2 -Co1 -As2 :	99.5(1)	Co1 -Co2 -As4 :	96.9(1)
As2 -Co1 -CCO1:	96.9(6)	As4 -Co2 -CCO2:	103.6(6)
CCO1-Co1 -CA1 :	104.3(8)	CCO2-Co2 -CA1 :	101.8(8)
CA1 -Co1 -Co2 :	49.1(6)	CA1 -Co2 -Co1 :	50.1(6)
Co2 -Co1 -CCO1:	152.9(6)	Co1 -Co2 -CCO2:	150.6(6)
Co1 -As1 -C13 :	116.4(5)	Co1 -As2 -C24 :	113.4(5)
Co1 -As1 -C1A1:	124.1(4)	Co1 -As2 -C2A1:	125.6(4)
Co1 -As1 -C1B1:	116.5(5)	Co1 -As2 -C2B1:	114.4(4)
C13 -As1 -C1A1:	99.1(7)	C24 -As2 -C2A1:	103.6(6)
C13 -As1 -C1B1:	100.6(7)	C24 -As2 -C2B1:	100.0(6)
C1A1-As1 -C1B1:	95.7(5)	C2A1-As2 -C2B1:	95.8(5)
Co2 -As3 -C13 :	113.1(6)	Co2 -As4 -C24 :	110.9(5)
Co2 -As3 -C3A1:	116.4(4)	Co2 -As4 -C4A1:	122.8(4)
Co2 -As3 -C3B1:	122.9(4)	Co2 -As4 -C4B1:	121.7(4)
C13 -As3 -C3A1:	101.0(7)	C24 -As4 -C4A1:	97.6(6)
C13 -As3 -C3B1:	102.6(7)	C24 -As4 -C4B1:	98.8(6)
C3A1-As3 -C3B1:	97.5(6)	C4A1-As4 -C4B1:	100.1(6)
As1 -C13 -As3 :	104.7(9)	As2 -C24 -As4 :	108.4(8)
CP11-CA1 -CA2 :	132(2)	CP21-CA2 -CA1 :	140(2)
CP11-CA1 -Co1 :	135(1)	CP21-CA2 -Co1 :	136(1)
CP11-CA1 -Co2 :	139(1)	CP21-CA2 -Co2 :	135(1)

TABLE IV-C-7 (CONT'D)

CA2 -CA1 -Co1 :	69(1)	CA1 -CA2 -Co1 :	70(1)
CA2 -CA1 -Co2 :	71(1)	CA1 -CA2 -Co2 :	68(1)
Co1 -CA1 -Co2 :	81(1)	Co1 -CA1 -Co2 :	80(1)
Co1 -CCO1-OCO1:	175(2)	Co2 -CCO2-OCO2:	172(2)
Cl1 -CS1 -CS2 :	112(3)	Cl2 -CS2 -CS1 :	102(3)

potentially very long cobalt-cobalt bond.

The two carbonyl ligands in $Co_2(CO)_2\cdot(PhCCPh)(Ph_2AsCH_2AsPh_2)_2$ are bent away from the acetylenic ligand by a slightly larger amount than in the phosphorus 1:1 complex. Angles CCO1-Co1-Co2 and CCO2-Co2-Co1 are 152.9° and 150.6° respectively. The OCO1-CCO1-Co1 and OCO2-CCO2-Co2 angles are 175° and 172° respectively and the oxygens are moved away from the 'side' of the molecule with the methylene carbon (C24) pointed 'upwards' toward the acetylene. From Figures IV-C-4 and IV-C-5 it can be seen that there are closer contacts between these oxygens and the phenyl groups attached to As2 and As4.

The CA1-CA2 bond is longer (1.37(3)Å) than in the phosphorus 1:1 complex (1.33(1)Å) but the difference is not significant within estimated standard deviations. The acetylenic phenyl groups in this complex are not oriented as they are in other diphenylacetylene dicobalt complexes. It has been observed that an angular difference of some 50-60° exists between the rings and the C-C≡C-C plane (Section A, Part 7). This angle was found to be 53.6° in the $Co_2(CO)_4\cdot(PhCCPh)(Ph_2PCH_2PPh_2)$ complex but in the arsenic 2:1 analog, both rings 'face away from' (see Figure IV-C-5) the As2-Co1-As1 'side' of the molecule with angles of 45° and 25° for the CP2 and CP1 rings respectively.

If Figures IV-C-2 and IV-C-5 are compared, it can be seen that the acetylenic phenyl ring that is above the bidentate bridging ligand in both complexes has the same orientation. This is probably a consequence of the similar positions of the phenyl groups 'B' attached to the group V_B atoms. In the case where only carbonyl ligands can influence the second acetylenic phenyl ring, in $Co_2(CO)_4\cdot(PhCCPh)(Ph_2PCH_2PPh_2)$, the angular difference of 53^o is preserved. However, the presence of the two 'B' phenyl rings attached to the second bridging bidentate ligand in $Co_2(CO)_2(PhCCPh)(Ph_2AsCH_2AsPh_2)_2$ does not permit the plane of the second acetylenic phenyl ring to lie between them and therefore the bend must occur.

Tables IV-C-8 and IV-C-9 give the intra- and intermolecular contacts to 3.0Å for the complex in the triclinic cell. Figure IV-C-6 gives a view of the unit cell down the *c* axis. The 1,2-dichloroethane molecule does not seem to play a significant role in determining the geometry of the complex. There is some interaction however since only the more polar form (*gauche*) of the 1,2-dichloroethane molecule exists in the crystal.

As a gas or in solution, 1,2-dichloroethane exists in both *gauche* and *trans* forms with 27% ± 5% of the molecules preferring the *gauche* conformation.[209] The angle between the planes Cl1-CS1-CS2 and the plane Cl2-CS2-CS1

TABLE IV-C-8

NON-BONDED INTRAMOLECULAR CONTACTS (Å) FOR DI-μ-[BIS(DIPHENYLARSINO)METHANE]-μ-(DIPHENYLACETYLENE)DICARBONYLDICOBALT · 1,2-DICHLOROETHANE SOLVATE

As1 -C1A2:	2.886	As1 -C1B2:	2.956
As1 -C1A6:	2.943	As1 -C1B6:	2.902
As1 -H1A2:	2.937	As1 -H1B2:	3.040
As1 -H1A6:	3.030	As1 -H1B6:	2.949
As1 -H131:	2.455	As1 -H132:	2.455
As2 -C2A2:	2.958	As2 -C2B2:	2.978
As2 -C2A6:	2.885	As2 -C2B6:	2.897
As2 -H2A6:	2.928	As2 -H2B6:	2.933
As2 -H241:	2.432	As2 -H242:	2.432
As3 -C3A2:	2.951	As3 -C3B2:	2.957
As3 -C3A6:	2.866	As3 -C3B6:	2.933
As3 -H3A6:	2.907	As3 -H3B6:	2.987
As3 -H131:	2.436	As3 -H132:	2.436
As4 -C4A2:	2.916	As4 -C4B2:	2.909
As4 -C4A6:	2.897	As4 -C4B6:	2.895
As4 -H4A2:	2.992	As4 -H4B2:	2.984
As4 -H4A6:	2.961	As4 -H4B6:	2.962
As4 -H241:	2.464	As4 -H242:	2.464
C13 -H1A6:	2.685	C24 -C4A1:	2.982
C13 -H3A2:	2.696	C24 -H2A2:	2.769
C13 -H3A2:	2.696	C24 -H2B2:	2.665
C13 -H3B2:	2.706	C24 -H4B6:	2.673
CA1 -CCO1:	2.898	CA2 -CCO1:	2.964
CA1 -CCO2:	2.879	CA2 -CCO2:	2.970
CA1 -CP12:	2.515	CA1 -HP12:	2.698
CA1 -CP16:	2.466	CA1 -HP16:	2.619
CA2 -CP22:	2.525	CA2 -HP22:	2.704
CA2 -CP26:	2.479	CA2 -HP26:	2.630
CA2 -CP11:	2.610		
CCO1-H1B6:	2.834	CCO2-H3A6:	2.772

TABLE IV-C-8 (CONT'D)

CCO1-HP26:	2.928	CCO2-H4B2:	2.672
OCO1-H2B6:	2.976	OCO2-H4B2:	2.788
Cl1 -CS2 :	2.693	Cl2 -CS1 :	2.552
CP11-H1B6:	2.780		
C1A1-C1B1:	2.920	C1A1-H1B2:	2.935
C1B2-H3B2:	2.611	C1A2-H2A6:	2.824
C1A6-H131:	2.840	C1B1-H132:	2.891
C1B2-H132:	2.921	C2A1-H241:	2.911
C2A1-H4A2:	2.809	C2A6-H2B6:	2.918
C2B1-H242:	2.893	C2B2-H242:	2.669
C3A1-C3B1:	2.968	C3B1-HP16:	2.780
C3A1-H131:	2.885	C3A2-H131:	2.923
C3B1-H132:	2.923	C3B2-H132:	2.717
C3B6-HP16:	2.888	C4A1-C4B1:	2.988
C4A1-H241:	2.807	C4A2-H131:	2.815
C4B1-H4A6:	2.641	C4B1-H242:	2.991
H1A2-H2A6:	2.993	H1A6-H4A2:	2.782
H1A6-H131:	2.124	H1A6-H132:	2.987
H1B2-H3B2:	2.775	H2A6-H2B6:	2.582
H1B2-H132:	2.566	H2A2-H241:	2.023
H2B2-H242:	1.953	H3A2-H131:	2.381
H3A2-H132:	2.699	H3A6-H3B6:	2.716
H3A6-H4B2:	2.543	H3B2-H132:	2.045
H4A2-H131:	2.683	H4A2-H241:	2.834
H4B6-H241:	2.397	H4B6-H242:	2.638
HP12-HP26:	2.259		

TABLE IV-C-9

INTERMOLECULAR CONTACTS (Å) FOR DI-μ-{BIS(DIPHENYLARSINO)-METHANE}-μ-(DIPHENYLACETYLENE)DICARBONYLDICOBALT SOLVATE.[a,b]

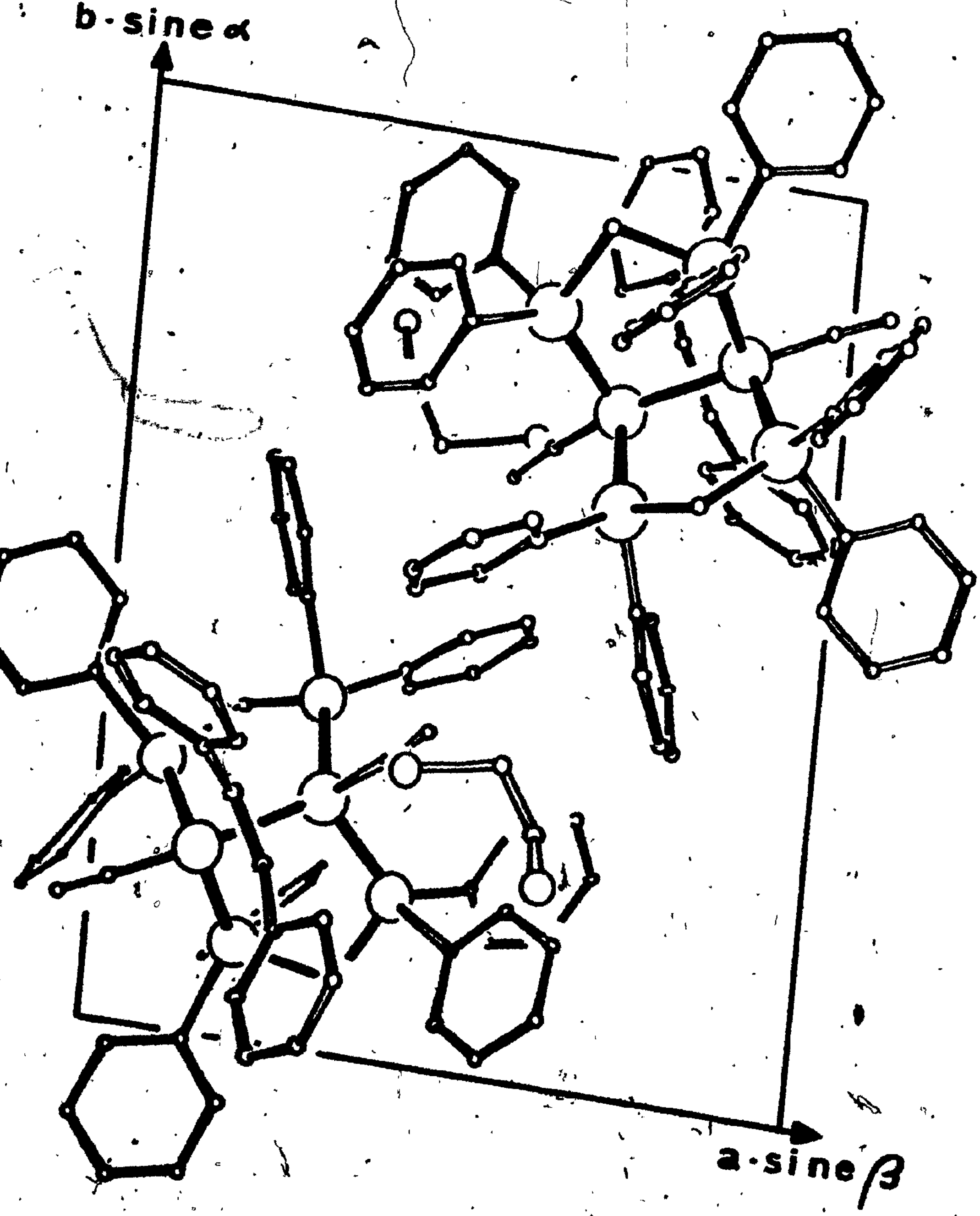
C2A2-H2B2:	2.862	IX	H2A2-H2B2:	2.147	IX
C2B2-H2A2:	2.778	IX	H2A2-H242:	2.894	IX
C3A2-H3B3:	2.995	VI	H2A3-H2B4:	2.567	IX
H2B5-C3A4:	2.883	IV	H2A3-HP23:	2.586	IX
C4B5-H3A4:	2.846	V	H2A4-H3B5:	2.751	I
CP21-H4B3:	2.877	VII	H2A4-H3B6:	2.743	I
CP22-H4B3:	2.784	VII	H2B4-H3A5:	2.403	IV
CP23-H2A3:	2.866	IX	H2B5-H3A4:	2.718	IV
CP25-H4A4:	2.976	III	H3A2-H3B3:	2.252	VI
OC01-H1A2:	2.844	XI	H3A3-H4B4:	2.632	V
OC01-H1A3:	2.994	XI	H3A4-H4A5:	2.987	V
OC02-HP23:	2.602	VII	H3A4-H4B5:	2.949	V
Cl1 -H4A3:	2.778	VIII	H3A5-H4A5:	2.658	V
Cl1 -HP12:	2.945	XI	H3A6-HP23:	2.820	VII
CS2 -H2B5:	2.970	XI	H3B4-HP13:	2.984	X
H1A3-H1B5:	2.987	XI	H4B2-HP23:	2.987	VII
H1A3-H1B6:	2.849	XI	HP14-HP15:	2.833	X
H1A4-H3B4:	2.369	I	HP25-H4A4:	2.705	III
H1A4-H3B5:	2.871	I	H1B3-H2B5:	2.643	XI
H1B4-H3A3:	2.937	VI	H1B4-H4B5:	2.621	II
H1B5-H2A5:	2.728	XI	H1B5-HP15:	2.814	X

a. Only atomic contacts less than 3.0Å are quoted.

b. The following transformations give the position of the second atom listed relative to the first which has the co-ordinates (x, y, z) listed in Table C-2, Appendix C:

I	$1 + x, y, z$	VI	$-x, 1 - y, -z$
II	$x, 1 + y, z$	VII	$-x, -y, 1 - z$
III	$x, y, 1 + z$	VIII	$1 - x, 1 - y, -z$
IV	$1 + x, y, 1 + z$	IX	$1 - x, y, 1 - z$
V	$-x, -y, -z$	X	$-x, 1 - y, 1 - z$
XI	$1 - x, 1 - y, 1 - z$		

Figure IV-C-6. Packing diagram for molecules of $Co_2(CO)_2 \cdot (PhCCPh)(Ph_2AsCH_2AsPh_2)_2$ and 1,2-dichloroethane in the triclinic cell as viewed down the *c* axis.


b·sine α
a·sine β

is 71° in the *gauche* rotational isomer and C-Cl and C-C distances are 1.78(1)Å and 1.48(3)Å as determined by electron diffraction. The Cl -C-C angles were measured and averaged $110 \pm 3^{\circ}$. In the *gauche* molecule observed in this crystal, the angle is 78° and the C-Cl and C-C distances are 1.80(4)Å and 1.44(6)Å respectively. The Cl -C-C angles average 107°.

The vibration ellipsoids for the atoms of the solvent molecule are very large as expected. Table IV-C-10 gives the major, median and minor axes as well as their direction cosines. The thermal ellipsoids of the atoms in the $Co_2(CO)_2(PhCCPh)(Ph_2AsCH_2AsPh_2)_2$ molecule are not unusual and the atoms do not appear to be appreciably anisotropic.

No appreciable change occurs in the acetylenic-cobalt bonding when the carbonyl ligands are successively substituted with group V_B ligands. Whatever changes do occur can be explained on the basis of steric repulsions caused by the bulky diphosphine and diarsine phenyl rings.

TABLE IV-C-10

THERMAL VIBRATION ELLIPSOIDS[a].- DI-μ-{BIS(DIPHENYLARSINO)-METHANE}-μ-(DIPHENYLACETYLENE)DICARBONYLDICOBALT

Atom	Axes[b]	Direction Cosines		
Co1	4.55	0.52921	0.24321	-.81289
	2.81	0.19767	0.89634	0.39686
	1.97	0.82515	-.37070	0.42627
Co2	4.28	0.64450	0.28228	-.71059
	2.58	0.14487	0.86744	0.47598
	2.17	0.75075	-.40972	0.51817
As1	4.14	0.44396	-.05984	-.89405
	3.15	0.64094	0.71847	0.27018
	2.73	0.62618	-.60298	0.35732
As2	4.73	0.59634	0.31993	-.73622
	2.78	0.28781	0.77095	0.56815
	1.79	0.74936	-.55070	0.36767
As3	4.85	0.77847	0.26121	-.57075
	3.29	0.14451	0.81029	0.56794
	2.11	0.61082	-.52460	0.59304
As4	4.36	0.66688	0.17769	-.72367
	2.72	0.13232	0.92748	0.34967
	2.07	0.73333	-.32894	0.59500
C13	4.09	0.47339	-.71930	0.50844
	3.94	0.67406	-.07576	-.73478
	3.22	0.56705	0.69056	0.44898
C24	7.87	0.71458	0.55352	-.42777
	4.50	0.34069	-.80944	-.47828
	0.99	0.61098	-.19603	0.76699
CA1	4.45	0.28099	-.24042	0.92911
	4.01	0.90529	0.38778	-.17344
	0.84	0.31859	-.88984	-.32661
CA2	7.37	-.44875	0.87521	-.18064
	3.13	0.88203	-.40131	0.24686
	2.00	-.14357	0.27011	0.95207
CO1	6.80	-.11053	-.40023	0.90972
	4.92	0.79921	0.50832	0.32073
	1.27	0.59080	-.76252	-.26368

TABLE IV-C-10 (CONT'D)

OCO1	9.93	0.56226	0.16713	-.80990
	6.64	0.72923	-.56205	0.39028
	3.65	0.38998	0.81004	0.43790
CCO2	5.43	-.02653	-.58529	0.81039
	4.32	0.99934	-.03579	0.00687
	0.59	0.02498	0.81003	0.58585
OCO2	9.83	0.02033	0.24051	0.97043
	7.89	0.15470	-.95970	0.23461
	2.36	0.98775	0.14536	-.05672
Cl1	18.26	0.73232	-.68092	-.00756
	12.57	0.63533	0.67921	0.36745
	8.46	-.24507	-.27390	0.93001
CS1	22.91	0.08347	0.88036	0.46691
	16.06	-.06664	-.46256	0.88408
	4.05	0.99428	-.10491	0.02006
CS2	56.28	0.75589	0.18549	0.62788
	11.04	-.22352	-.82828	0.51379
	1.86	0.61536	-.52871	-.58463
Cl2	39.14	0.88734	-.26407	-.37801
	25.04	0.46033	0.55494	0.69292
	11.64	0.02679	-.78887	0.61398

[a] Given in the order of major, median and minor axes.

[b] Axes lengths are in units of B where the root mean square displacement $(\overline{U}^2)^{\frac{1}{2}} = (B/8\pi^2)^{\frac{1}{2}}$.

CHAPTER V. STUDIES OF SOME π-(ARENE)ENNEACARBONYLTETRACOBALT(0) CLUSTERS AND THE CRYSTAL AND MOLECULAR STRUCTURES OF π-(XYLENE)ENNEACARBONYLTETRACOBALT(0) AND π-(BENZENE)ENNEACARBONYLTETRACOBALT(0).

SECTION A. INTRODUCTION

1. The Polarization Complexes

One of the most interesting features of benzenoid-metal complexes is the degree to which the intrinsic D_{6h} symmetry of the arene does or does not change upon complexation. In 1950, Rundle and Goring[210] published a paper concerning a benzene silver(I) perchlorate complex in which, according to the more complete crystallographic investigation that followed,[211] the benzene rings 'sandwich' asymmetrically-distributed silver ions. It was reported that the arene C-C bonds closest to the Ag^+ ions were shorter (1.35(2)Å) than the others (1.43(1)Å). To explain this observation, the authors claim that the positively-charged silver ion polarizes the π electrons in the arene. This increases the electron density on the carbon atoms adjacent to the ionic nucleus to the detriment of the other carbon atoms.

A somewhat more accurate description of the bonding in aromatic-silver(I) perchlorate complexes was developed from a systematic X-ray crystallographic study undertaken by E.L. Amma. Some complexes with a 2 to 1 ratio of aromatic to $AgClO_4$ that were investigated include *o*-xylene,[212] *m*-xylene,[213] *p*-xylene,[214] and cyclohexylbenzene.[215] Also examined were 1 to 1 complexes of dibenzyl,[216] indene,[217] acenaphthene[218] and acenaphthylene[218] as well as (naphthylene)$\cdot 4AgClO_4 \cdot 4H_2O$[219] and (anthracene)$\cdot 4AgClO_4 \cdot H_2O$.[219]

Most of these structures consist of sheets of $AgClO_4$ separated by arenes. The silver ion is bonded disymmetrically to all aromatic moieties, except in the case of the naphthalene complex, with a 'constant' closest Ag-C approach of 2.47 ± 0.03Å. The second closest Ag-C distance is quite variable in these complexes (2.51→2.98Å).

Since the sum of covalent radii gives a Ag-C bond length of 2.30Å,[220] the bonding in the arene-silver(I) perchlorate complexes is not of a formal nature. There are two bonding modes operating in these compounds according to an analysis of the X-ray crystallographic data obtained by Amma. First, the arene acts as an electron donor to the metal ion M. This type of bonding would require M to be positioned directly above one of the carbon atoms of the ring at a position of highest π electron density.

Back-donation from metal ion to the arene is also important in explaining the bonding. The best overlap between filled d orbitals and the antibonding π^* molecular orbitals of the aromatic moiety results when the metal is in the π cloud of the arene equidistant between two adjacent carbon atoms. It can be seen that a compromise between these two types of bonding will result in the observed geometries, *i.e.* the metal ion between two adjacent carbon atoms of the aromatic part of the structure but closer to one than the other.

Although these complexes have been known for some time,[221] X-ray crystallographic investigations, especially in the last five years, have given a better understanding of the types of bonding involved. The last review of these type of compounds appeared in 1966.[222]

Polarized bonding of π arene systems can be found in another structure: that of hexathiocyanatocobalt dimercury.[223] In this structure, benzene molecules separate sheets of $Hg_2Co(SCN)_6$. The authors record a variation in the three crystallographically-independent

C-C distances in the order of 0.1Å. In contrast with the benzene-silver(I) perchlorate complex discussed earlier, the C-C bond closest to the mercury ion in hexathiocyanato-cobalt dimercury is the longest.

Dines and Bird[224] published a preliminary report on aromatic complexes of copper(I) trifluoromethane-sulphonate. The X-ray structure determination of the benzene complex is reported to show two copper atoms π bonded to each benzene ring with an average Cu-C distance of 2.21Å. The accuracy of the results is not good due to poor crystal quality. Even if the C-C distances vary by as much as 0.2Å in the benzene ring (1.48, 1.48, 1.28, 1.39, 1.28 and 1.35Å; e.s.d. 0.04Å), no arguments can be presented for or against complete retention of the fully-delocalized π system in benzene.[225]

Gilson[226] has shown, in a solid state nmr study, that there appears to be free rotation of the benzene moiety at room temperature in the above compound. Gilson and McDowell[227,228] have also studied the nmr spectra of the benzene-silver(I) perchlorate complex described earlier. Their conclusion of a "more-or-less" freely rotating benzene has been challenged by Smith[229] who claims that because of the limitations of the nmr time scale, the difference between high disorder and free rotation in the solid state cannot be ascertained using this technique.

The distances between the copper ion and the two closest benzene carbon atoms are 2.15 and 2.30Å in the complex (benzene)$Cu^{I}AlCl_4$.[230,231] These bond lengths are very close to the Cu-C single bond length of 2.12Å[220] and this suggests a rather substantial metal ion-aromatic interaction. The symmetry of the copper(I) environment is distorted tetrahedral and this suggests that an sp^3 hybrid orbital on copper is acting as the acceptor for aromatic π electrons.

There is, in this excellent structure determination, good indication of an important distortion towards a hexatriene system implying that one of the Kékulé structures of benzene has been frozen out. Indeed the C-C bond lengths are, in sequence around the ring, 1.26(5), 1.41(5), 1.25(4), 1.37(4), 1.29(4), and 1.40(5)Å. A similar variation exists in the structure of (benzene)-$AgAlCl_4$[232] but the estimated standard deviations in this structure are very large due to bad disordering within the crystal.

It will be noticed that all structures mentioned above showed poor accuracy largely due to their nature as loosely-bound polarization or charge transfer complexes. Large thermal vibrations result from this type of bonding which cause large errors in the determination of atomic positions. This, coupled with the fact that atomic parameters of light atoms in a structure containing heavy atoms generally are not very accurate permit questioning of any arguments about the bonding based on the geometries recorded. It seems unquestionable however that some trends are real. It will be instructive now to look at some more strongly-held valency compounds of the transition metal arenes.

2. <u>The Bis-arene Complexes</u>

What follows is not intended to be an exhaustive survey of the literature of transition metal π arene complexes. Many general reviews exist as well as three surveys of the structure of these compounds.[222,233-245] The intention here is to provide background information concerning the formation of these complexes with a somewhat more intensive treatment of their structural properties and bonding.

a) <u>Synthesis</u>

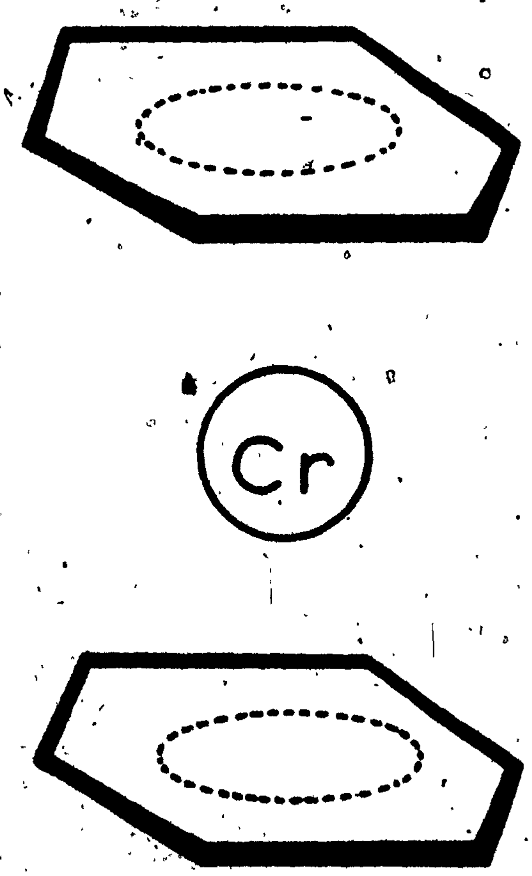
The first transition metal π arene synthesized was not recognized as such until thirty-five years later.

In 1919, Hein[246] isolated, from the Grignard reaction of phenylmagnesium bromide and chromium(III) trichloride in ether solution, a compound which he claimed to be pentaphenylchromium(I) bromide. Soon, a vast chemical literature developed surrounding various polyphenyl chromium compounds largely fed by the continued work of Hein.

The chemistry of these compounds displayed several severe inconsistencies with their proposed structures. The nature of these differences has been adequately reviewed by Zeiss.[233] It will be sufficient here to state that various anomalous chemical as well as physical properties of the polyphenyl chromium compounds led Tsutsui and Zeiss to examine the products of their reductive degradation by lithium aluminum hydride.

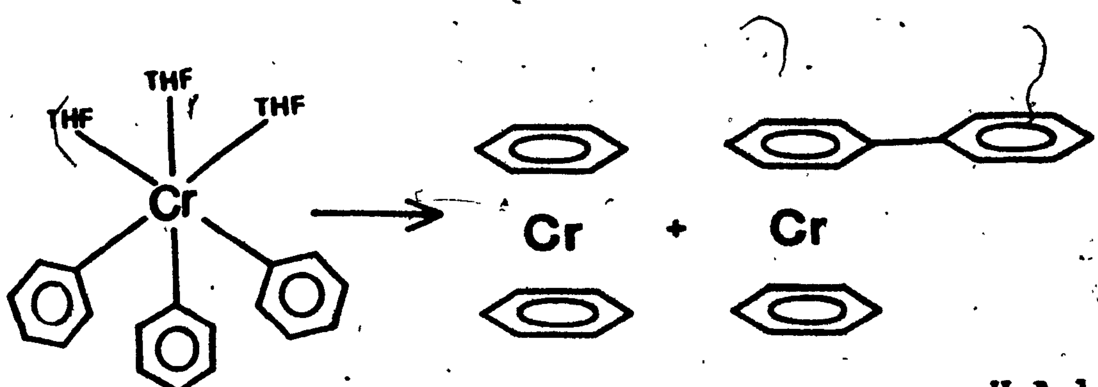
As a result of this work, a correction was made to the formulation of these complexes. Zeiss, Tsutsui and Onsager[247-248] proposed a biconoidal sandwich π structure for this type of complex which now explained all the heretofore inexplicable magnetic, spectroscopic and chemical data (Figure V-A-1). The concept however was viewed with considerable apprehension by some, including the referees of an abortive attempt at the publication of a later-to-appear Zeiss-Tsutsui paper,[249] who grieved at the loss of the benzenoid resonance energy in bonding to an inorganic nucleus. It would remain for others to show that

Figure V-A-1. The proposed biconoidal sandwich π structure for the bis-arene chromium complexes.



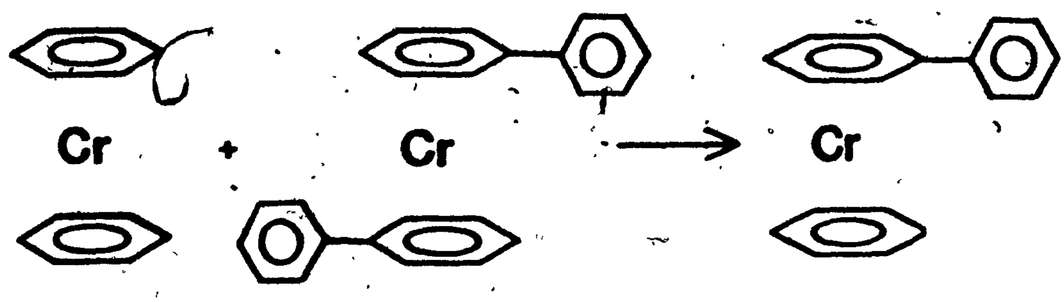
this loss was minimal.

Fischer and Hafner[250-251] devised a method of synthesizing bis-arene complexes involving the reduction of chromium(III) trichloride by aluminum powder at 150°C in the presence of an arene. Other synthetic routes have since been devised for the bis-arene complexes. The Fischer-Hafner synthesis has been adapted to use trialkylaluminum as the reducing agent instead of aluminum powder. Another synthetic procedure involves the σ to π rearrangement of triphenylchromium(III)tetrahydrofuranate.[252-253] Such a rearrangement occurs when the tetrahydrofuran molecules are removed 1) by heating to 60°C at atmospheric pressure, 2) *in vacuo* or 3) by treating the crystalline tetrahydrofuranate with diethylether.[254]



V-A-1

Of limited use is the redistribution method of preparing new bis-arene complexes. Two π arene complexes are mixed and the materials recovered are redistribution products as illustrated in Equation V-A-2. Studies in the cyclic trimerization of acetylenes have resulted in the isolation of intermediate bis-arene complexes. Such reactions will be discussed in another section of this introduction.



V-A-2

Some bis-arene complexes can be prepared by directly combining the arene and the metal in its pure state. Co-condensation of benzene and chromium atoms has given dibenzenechromium(0) in 60% yield.[255] It is difficult by conventional methods to synthesize bis-arene complexes of halogen-substituted arenes because of the strongly electron withdrawing effects of the substituents. The π electron density of the aromatic moiety is critical in determining the degree of formation of these complexes.[256] Very recently the co-condensation method was used to synthesize chlorobenzene, fluorobenzene and *p*-difluorobenzene bis-arene chromium compounds.[257]

In but a very few years the number of bis-arene complexes of chromium and other elements proliferated mainly owing to their function as intermediates in the cyclic trimerization of acetylenes and to the interest many investigators had in their structure and bonding.

b) Structure of Dibenzenechromium(0)

Ruch[258-261] put forth the hypothesis that the bonding in bis-arene chromium complexes could be explained in terms of the following formulation. Three co-ordinate covalent bonds are formed between the three pairs of π electrons in each ring and the chromium metal. If this hypothesis is correct, it should lead to a threefold distortion of the benzenoid moiety as compared to the free arene. Fischer and Böttcher[262] reinforced this frozen-out Kékulé structure argument by explaining the greater stability of dimesityleneiron(II) compared to dibenzeneiron(II) in terms of its intrinsic threefold symmetry.

An attempt at establishing the structure of dibenzenechromium by X-ray crystallography was effected by Weiss and Fischer in 1956.[263] This investigation was the first of many attempts to determine unambiguously whether a localized or, alternatively, a delocalized bonding scheme was operative in this complex. The molecule crystallizes in a cubic unit cell (Pa3, No. 205) and is constrained to a chromium atom position coincident with a center of inversion.

Jellinek[264] and Cotton *et al.*[265] were of opposing view as to their interpretation of the crystallographic data. Ibers[266] used Hamilton's R factor test[267] to justify Cotton's D_{6h} model for the complex. Zeiss *et al.*[222] concurred from their further refinement of opposing sets of data. Insistently, Jellinek[268] published another paper reporting the results of full anisotropic refinement of his data to lead to his original observation of a D_{3d} model for the compound.

A major point made by Jellinek in this paper is the limitation placed on the accuracy of any structure determination of dibenzenechromium(0) executed at room temperature. Thermal motion of the atoms in the rings decrease the probability of an accurate determination of positional parameters. We have seen how this factor plays a major role in the loosely-bound polarization complexes of arenes with silver, mercury and tin. The effect is less in this valency compound of chromium but it is sufficient to cause considerable doubt about the interatomic distances derived. A low temperature study of dibenzenechromium(0) was warranted and this was effected by Keulen and Jellinek in 1966.[269]

The data were collected at 100°K and for 486 independent reflections, the final R factor was 3.1%. The calculated bond lengths were corrected for the thermal motion corresponding to the libration of the rings and the crystallographically-independent bonds were 1.420(3) and 1.419(3)Å. The Cr-C distances were also equal within the standard deviations at 2.143(2) and 2.140(2)Å. No significant deviation from D_{6h} molecular symmetry could thus be found.

A myriad of physical methods other than X-ray crystallography have been used to determine the structure of bis-arene chromium complexes. In 1965, Haaland reported the results of an electron diffraction study of dibenzene-chromium(0).[270] An analysis of the radial distribution curve was compatible with a D_{6h} symmetry model in which the C-C distance is 1.423 ± 0.002Å and the Cr-C distance is 2.150 ± 0.002Å.

Distortion of the ligands in dibenzene-chromium(0) was investigated by solid state vibrational analysis. Fischer and Fritz first presented evidence for threefold distortion of the benzene rings.[238] Fritz *et al.* then contradicted this argument.[271] The solution infrared spectrum could be fully explained based on a D_{6h} model. It was claimed that crystal forces may be responsible for the distortions observed by solid state infrared studies and some of the X-ray crystallographic structure investigations.

Far infrared studies by Fritz and co-workers attempted to show[272,273] that the crystal forces and site symmetries in the solid state are not sufficient to account for the frozen Kekulé type structure found for these bis-arene complexes. The potassium bromide pellet infrared spectrum of dibenzenechromium(0)[274] is however different in the number and the positions of the absorption intensities from the infrared spectrum of pure dibenzenechromium(0).[275] It is not very easy to explain these differences without appealing to the influence of crystal forces.

Nagi, Stafford and Schäfer[276] found, by a careful study of the vapour phase infrared spectrum of dibenzenechromium(0), that deviations from D_{6h} symmetry must be very small if at all existent. Using the values determined by Schäfer, Southern and Cyvin,[277] Schäfer *et al.*[278] have executed a partitioned normal co-ordinate analysis on dibenzenechromium(0) and deuterated dibenzene-chromium(0).[279] These studies point emphatically to D_{6h} symmetry for these complexes in the vapour phase.

There appears to be free rotation at room temperature of the rings in dibenzenechromium(0) from a cursory study of the nmr line shape variations with temperature.[280] Further investigation of the freedom of rotation in these complexes was carried out by Andrews *et al.*[281] This study showed that free rotation of the arene ligands in the complex best fits the observed entropy.

Qualitative theoretical approximations made by Ruch[259] and Fritz *et al.*[282] to a D_{3d} model for the bis-arene metal complexes must surely now be examined with but historical interest. It seems very likely that crystal forces, bad data and underestimated standard deviations have been responsible for masking the true nature of the bonding in these compounds. It appears, from the very meticulous low-temperature X-ray structure determination[269] and the careful study of spectroscopic evidence obtained in the vapour phase,[279] that dibenzenechromium(0) can be experimentally described as a sandwiched eclipsed biconoidal structure in which all benzene C–C distances are equal at 1.420(3)Å and all Cr–C distances are equal at 2.141(2)Å.

c) Bonding in Dibenzenechromium(0)

The discovery of the bis-arene metal complexes presented a considerable challenge to the theoretical chemist in order to explain their existence. Indeed, π bonded arene systems had heretofore never been seen, so it was only natural that the development of bonding theories should parallel the rapidly-increasing experimental evidence on these compounds.

The first discovery of the nature of these complexes as biconoidal π sandwiched chromium atoms[247] led scientists to assume a fixed Kékulé structure for each benzene ring with three co-ordinate covalent bonds to the central metal atom (Figure V-A-2). This implied an octahedral co-ordination about the metal (d^2sp^3 hybridization) and overall D_{3d} symmetry.

The magnetic properties of the bis-arene complexes were accounted for in this valence bond approach. Dibenzenechromium(0) was indeed observed to be diamagnetic and a similar treatment for the neutral dibenzenevanadium(0) would result in the paramagnetism observed experimentally.

A molecular orbital calculation on the dibenzenechromium(0) complex was performed by E.M. Shustorovich and M.E. Dyatkina in 1960.[283-285] The ring molecular orbitals used were linear combinations of the carbon atomic $2p\pi$ orbitals (Figure V-A-3). D_{6h} symmetry was assumed and distances of 1.40Å for C-C and 2.19Å for Cr-C were used in the calculation of the energies of the twenty-one molecular orbitals of dibenzenechromium(0). An energy level diagram is shown in Figure V-A-4.

Figure V-A-2. A valence bond treatment of the dibenzene-chromium(0) complex.

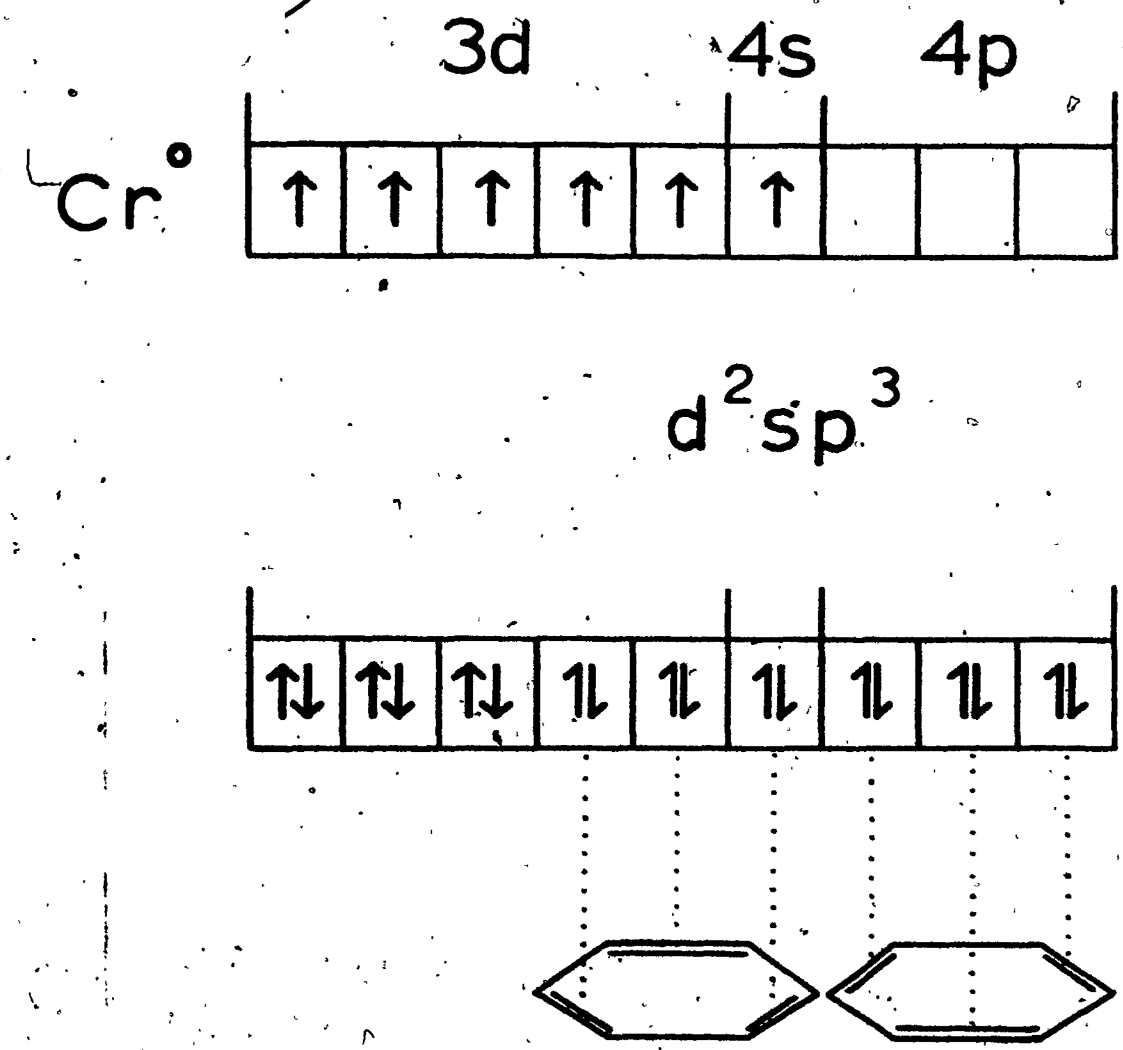

3d
4s
4p
Cr°
d²sp³

Figure V-A-3. Molecular orbitals of benzene used in forming the dibenzenechromium(0) complex.

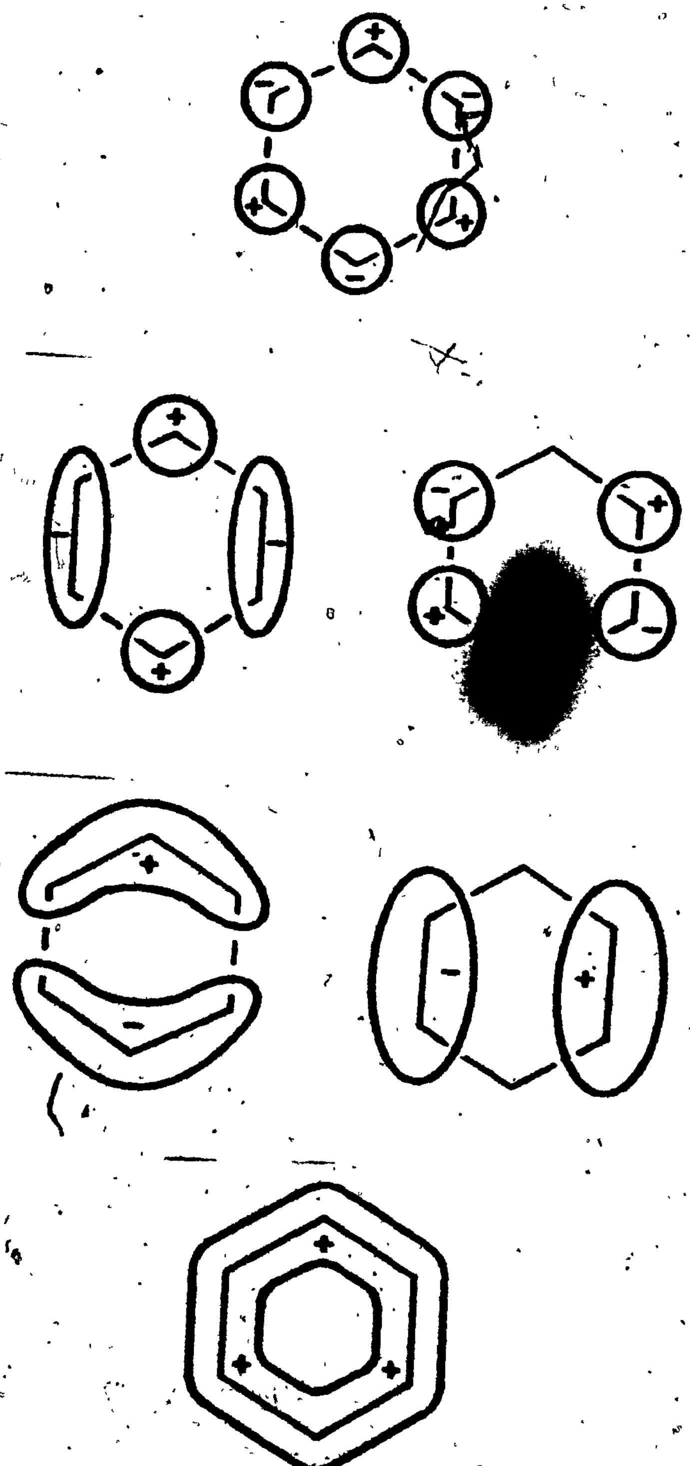
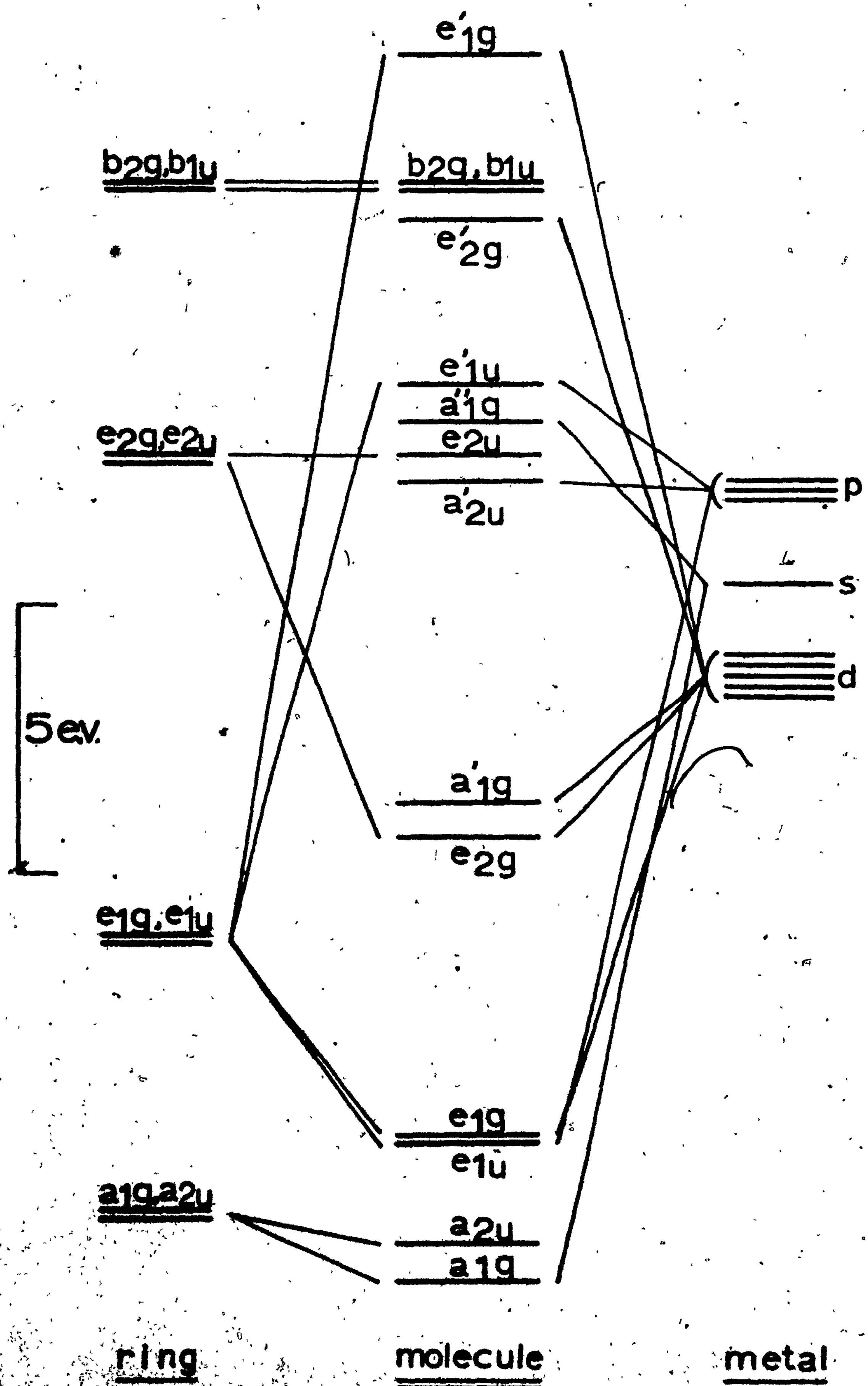


Figure V-A-4. The energy level diagram from the molecular orbital treatment of dibenzenechromium(0) by Shustorovich and Dyatkina (from Reference 285, page 176).



e'_{1g}
b_{2g}, b_{1u}
b_{2g}, b_{1u}
e'_{2g}
e'_{1u}
a'_{1g}
e_{2u}
a'_{2u}
e_{2g}, e_{2u}
p
s
d
5 ev.
a'_{1g}
e_{2g}
e_{1g}, e_{1u}
e_{1g}
e_{1u}
a_{1g}, a_{2u}
a_{2u}
a_{1g}
ring
molecule
metal

According to the scheme devised by Shustorovich and Dyatkina, in neutral molecules the metal atom carries a net positive charge. This implies that electronic charge is transferred from the metal toward the rings in a dative back-bonding type of effect. This effect counteracts the loss of the π electron density of the benzenoid moiety due to its Lewis base six electron donor ability. The resonance energy of the benzene nucleus is maintained, a problem which had preoccupied earlier workers.

The retention of the resonance energy of benzene in dibenzenechromium(0) has been shown by a comparison of the ultraviolet spectra of the free ligand and the complex.[286] A detailed molecular orbital calculation for the molecule favours complete delocalization of the ring π electrons.[287]

d) Other Bis-arene Complexes

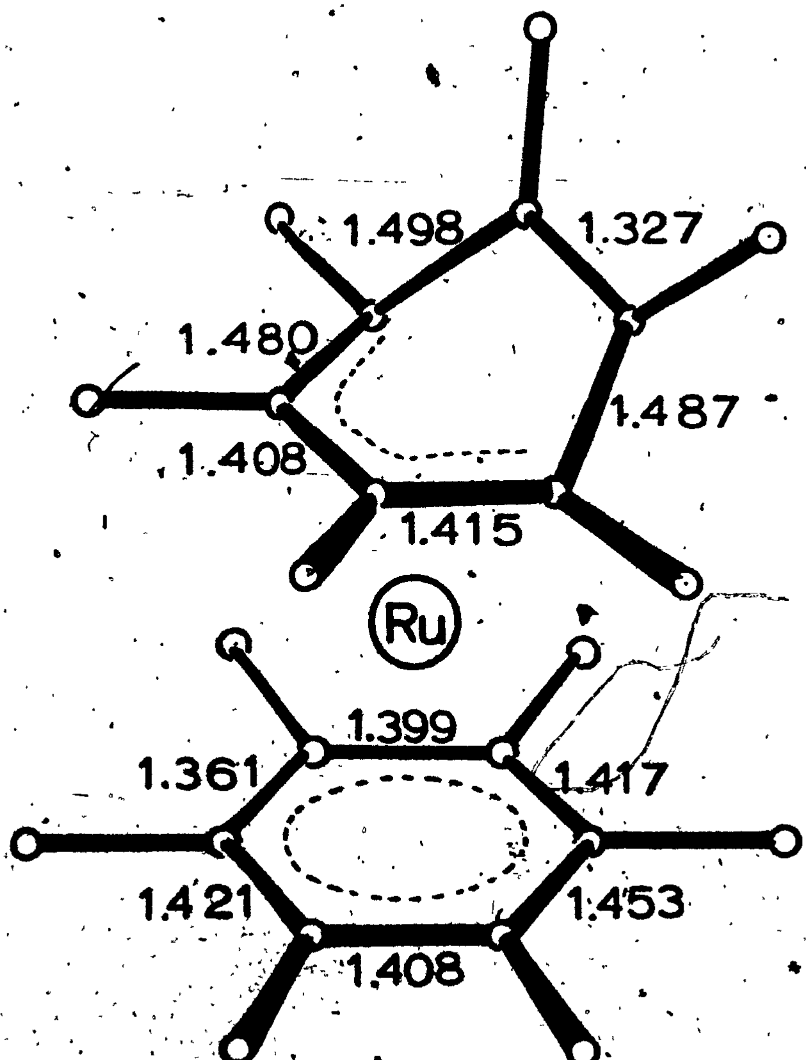
Dibenzenemolybdenum(0) and dibenzenetungsten(0) have been synthesized[288,289] as well as the sandwiched benzene complex of vanadium. The far-infrared spectrum of this complex has been compared to that of its chromium analog.[272]

Zeiss and Tsutsui have patented the synthesis of several bis-arene complexes including dihexamethylbenzenecobalt(0)[290] and the tetraphenylborate salt of dihexamethylbenzenemanganese(I).[291] The hexafluoroplatinate salts of dihexamethylbenzenerhodium(I) and dihexamethylbenzenerhodium(II) have also been synthesized[292] and studied by spectroscopic means. In 1970, Fischer and Elschenbroich[293] showed that the arene structure in the diamagnetic complex dihexamethylbenzeneruthenium(0) is not planar. This conclusion was reached by studying the methyl resonances by proton nmr.

The following year a single crystal X-ray structure analysis confirmed this result.[294] Although one of the two hexamethylbenzene rings is planar, the other ring is bent as shown in Figure V-A-5.

The authors propose that the distortion of the ring in this complex is due to the fact that, if bonds were formed equally with both rings, twelve electrons would complement the eight electrons in the ruthenium(0) valence shell. This would give two electrons too many to comply with a noble gas configuration. Bond lengths in this complex indicate four rather than six carbons are bonded to the central metal atom in the distorted ring. Evidence has also been gathered to show that dihexamethylbenzenecobalt(0) is bonded in a similar fashion.[295]

Figure V-A-5. Bonding in dihexamethylbenzeneruthenium(0). The bond lengths are shown in Å with no distance with an e.s.d. greater than 0.012Å.



1.498
1.327
1.480
1.487
1.408
1.415
Ru
1.399
1.361
1.417
1.421
1.453
1.408

The ditoluenechromium cation has been subject to two crystallographic structure determinations and the aromatic rings have been shown to be planar. The structure of the iodide complex[296-298] shows that the cation has 2/m symmetry with an average C-C ring bond length of 1.42 ± 0.03Å.

Structures of 1) the 1 to 2 complex of ditoluenechromium(I) and 7,7,8,8-tetracyanoquinodimethane[299] and 2) the 1 to 1 complex of ditoluenechromium(I) and the same anion[300] have been reported recently. The cationic species in the latter complex is in the eclipsed conformation with the methyl of ring two lying under the *meta* position of ring one. This should be contrasted with the *para* orientation of the ditoluene iodide species discussed above. The 1 to 2 complex exhibits a prismatic *trans* configuration for the toluene rings of the cation.

Using Fischer's method, Allegra *et al.*[301] synthesized an unusual transition metal bis-arene complex. $AlCl_3$, $PdCl_2$ and aluminum powder suspended in 50 ml of anhydrous benzene were heated. The resulting brown suspension was filtered hot under nitrogen and crystals were obtained from slow cooling of the filtrate. The complex obtained was reported to have the formula $(PdAl_2Cl_7C_6H_6)_2$. When a lesser amount of aluminum trichloride was used, a complex of the formula $(PdAlCl_4C_6H_6)_2$

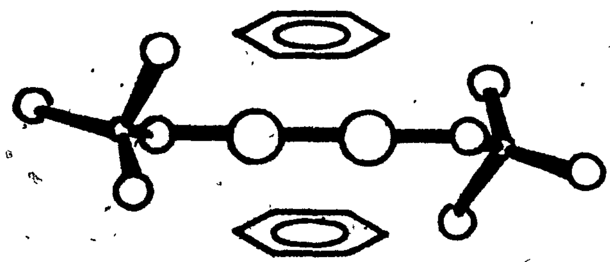
was obtained. Both these complexes have been the subject of X-ray crystallographic analysis.[302]

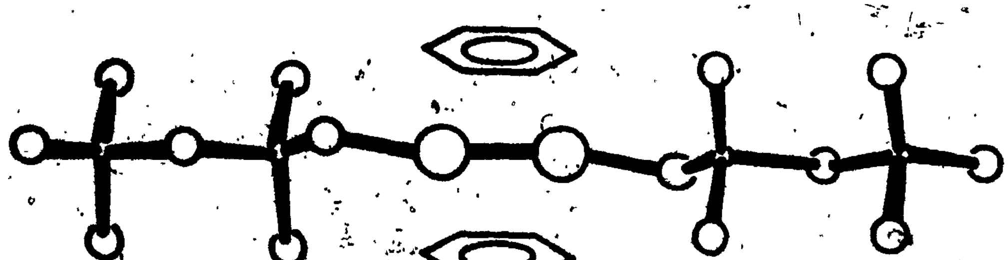
In these complexes, two benzene moieties sandwich a Pd-Pd bond. Figure V-A-6a illustrates the bonding in $(PdAl_2Cl_7C_6H_6)_2$. Figure V-A-6b does the same for $(PdAlCl_4C_6H_6)_2$. Not all the carbon atoms of the benzene are equally involved in bonding to the palladium atoms in these complexes. Although the bond distances in the arene cannot be used as a measure of the degree of localized bonding due to their large average standard deviations, the deviations from planarity of the rings are an indication of the decreased aromaticity. Bonding in these complexes is, to say the least, unusual and more work will surely be needed to clarify it.

Another compound to be synthesized by Fischer's method was made from UCl_4 rather than $PdCl_2$.[303] Analysis showed the compound to be $UAlCl_{12}C_6H_6$. A single crystal X-ray crystallographic investigation showed a structure which can be described as three $AlCl_4$ units each bonded to uranium through two chlorine bridges. The benzene moiety is π bonded in the same way as in the bis-arene complexes discussed above. The arene seems to be bonded in a symmetric fashion judging from the equivalence of the six metal-to-carbon distances reported.

Figure V-A-6a. The complex $(PdAl_2Cl_7C_6H_6)_2$.

Figure V-A-6b. The complex $(PdAlCl_4C_6H_6)_2$.





Various ruthenium, rhodium and iridium π arene complexes have been synthesized recently. L.M. Haines has been responsible for reporting the preparation of many complexes of rhodium and iridium with tetraphenylboron in which one of the phenyl groups is π bonded to the metal. Neutral complexes of the general type $Rh\{P(OR)_3\}_2B(C_6H_5)_4$ have been obtained by the decomposition of the ionic $Rh\{P(OR)_3\}_4B(C_6H_5)_4$ and $Rh\{P(OR)_3\}_5B(C_6H_5)_4$ species.[304] These have been studied by nmr spectroscopy[305] and the results indicate that the molecule has the same structure in solution as in the solid state.

The X-ray single crystal structure determination of the complex $Rh\{P(OCH_3)_3\}_2B(C_6H_5)_4$ was reported by Nolte, Gafner and Haines [306] in 1969. The π bonded phenyl ring in the tetraphenylboron unit is in the boat conformation.

A *pentahapto*cyclopentadienyl-*hexahapto*phenyl-triphenylborate complex of ruthenium has also been synthesized and studied by infrared spectroscopy.[307] Sanders [308] has very recently reported the preparation of a tris(tri-phenylphosphine)ruthenium hydride in which one of the triphenylphosphine ligands is not bonded through the phosphine but is bonded through the *hexahapto*- interaction of one of the phenyl moieties.

A cycloocta-1,4-dienylhexakis(trifluoromethyl)benzenenickel complex has been synthesized[309] recently. The bonding has not been examined by X-ray analysis but it may well be the same as that in the (*pentahapto*cyclopentadienyl)-1,2,3,4-*tetrahapto*hexakis(trifluoromethyl)-benzenerhodium(0) complex reported by Churchill and Mason.[310,311] The bonding, determined by single crystal structure analysis, seems to involve but four of the six arene carbon atoms. The arene is folded along a line joining the 1 and 4 carbon atoms and the angle formed between the two halves of the ring is 132.1°. The C_5-C_6 bond of the portion of the ring not involved in the π bond to rhodium is 1.306(19)Å commensurate with full double bond character. This type of bonding has been seen above for the dihexamethylbenzeneruthenium(0) structure.

A summary of the X-ray crystallographically-determined bond lengths for those complexes discussed in the foregoing which were so investigated are found in Table V-A-1.

3. The Transition Metal Carbonyl Arene Complexes

a) Arene Chromium Tricarbonyls

Arene chromium tricarbonyls can be synthesized

TABLE V-A-1

INTERATOMIC DISTANCES IN SOME BIS-π-ARENE COMPLEXES[b]

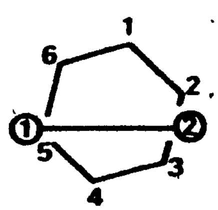
COMPOUND	METAL-ARENE DISTANCE (A)	ARENE CARBON-CARBON DISTANCES (A)	REMARKS AND REFERENCE
Dibenzene-chromium(0)	$M-C_a$: 2.135(10) $M-C_b$: 2.132(10) $M-R^a$: 1.613(07)	C_a-C_b: 1.45 C_b-C_a: 1.36	Jellinek First iso. Room Temp. 264
	$M-C_a$: 2.143(08) $M-C_b$: 2.132(08) $M-R^a$: 1.614(06)	C_a-C_b: 1.436(12) C_b-C_a: 1.366(12)	Jellinek 1st aniso. Room Temp. 268
	$M-C_a$: 2.147(02) $M-C_b$: 2.144(02) $M-R^a$: 1.609(01)	C_a-C_b: 1.420(03) C_b-C_a: 1.419(03)	Jellinek Low Temp. 269
		C_x-C_y: 1.387(17)	C.D.W. 265
	$M-C$: 2.150(02)	C_x-C_y: 1.423(02)	Electron Diff. 270
$(PdAl_2Cl_7C_6H_6)_2$ 	M_1-C_1: 3.16(03) M_1-C_2: 3.46(03) M_1-C_3: 3.20(03) M_1-C_4: 2.62(03) M_1-C_5: 2.20(03) M_1-C_6: 2.49(03) M_2-C_1: 2.81(03)	C_1-C_2: 1.42(05) C_2-C_3: 1.38(05) C_3-C_4: 1.44(05) C_4-C_5: 1.41(05) C_5-C_6: 1.37(05) C_6-C_1: 1.39(05)	Only one set of the two disordered ring positions is given here 302

TABLE V-A-1 (CONT'D)

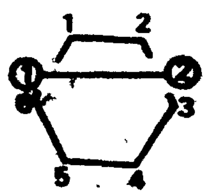
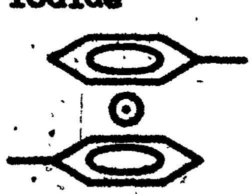
	M_2-C_2: 2.22(03)		
	M_2-C_3: 2.31(03)		
	M_2-C_4: 3.00(03)		
	M_2-C_5: 3.43(03)		
	M_2-C_6: 3.30(03)		
$(PdAlCl_4C_6H_6)_2$	M_1-C_1: 2.37(02)	C_1-C_2: 1.38(04)	302
	M_1-C_2: 3.03(02)	C_2-C_3: 1.40(04)	
	M_1-C_3: 3.49(02)	C_3-C_4: 1.38(04)	
	M_1-C_4: 3.38(02)	C_4-C_5: 1.37(04)	
	M_1-C_5: 2.77(02)	C_5-C_6: 1.41(04)	
	M_1-C_6: 2.26(02)	C_6-C_1: 1.45(04)	
	M_2-C_1: 3.03(02)		
	M_2-C_2: 2.37(02)		
	M_2-C_3: 2.27(02)		
	M_2-C_4: 2.77(02)		
	M_2-C_5: 3.31(02)		
	M_2-C_6: 3.51(02)		
$UAl_3Cl_{12}C_6H_6$	M -C_1: 2.91	C_x-C_y: Not quoted	303
	M -C_2: 2.91		
	M -C_3: 2.92		
	M -C_4: 2.92		
	M -C_5: 2.92		
	M -C_6: 2.91		
Ditoluene-chromium(I) Iodide	M -C_1: 2.088(04)	C_x-C_y: Average 1.42 ± 0.03	297
	M -C_2: 2.089(04)		
	M -C_3: 2.089(04)		
	M -C_4: 2.079(04)		
	M -C_5: 2.089(04)		
	M -C_6: 2.082(04)		

TABLE V-A-1 (CONT'D)

Ditoluene-chromium(I) T.C.N.Q.$^-$ 1:1 Adduct	$M-C_x$: Average	2.11 ± 0.03	C_x-C_y: Average	1.38 ± 0.04	300
Ditoluene-chromium(I) T.C.N.Q.$^{\bullet}$/T.C.N.Q.$^-$ 2:1 Adduct	$M-C_x$: Average	2.18 ± 0.03	C_x-C_y: Average	1.40 ± 0.04	299
$Rh\{P(OCH_3)_3\}_2 \cdot B(C_6H_5)_4$	$M-C_1$:	2.41(02)	C_1-C_2:	1.41(03)	Bent Ring 306
	$M-C_2$:	2.30(02)	C_2-C_3:	1.42(03)	
	$M-C_3$:	2.30(02)	C_3-C_4:	1.42(03)	
	$M-C_4$:	2.40(02)	C_4-C_5:	1.44(03)	
	$M-C_5$:	2.31(02)	C_5-C_6:	1.39(03)	
	$M-C_6$:	2.33(02)	C_6-C_1:	1.44(03)	
Perfluoro-hexamethyl-benzene-cyclopenta-diene-rhodium(0)	$M-C_1$:	2.150(18)	C_1-C_2:	1.477(20)	Ring bent along line joining C_1 to C_4 311
	$M-C_2$:	2.064(18)	C_2-C_3:	1.424(19)	
	$M-C_3$:	2.109(14)	C_3-C_4:	1.528(21)	
	$M-C_4$:	2.119(15)	C_4-C_5:	1.481(25)	
	$M-C_5$:	3.010(18)	C_5-C_6:	1.306(19)	
	$M-C_6$:	3.052(18)	C_6-C_1:	1.501(23)	
Bis(hexa-methylbenzene)-ruthenium(0)	$M-R_1^a$:	1.75	C_1-C_2:	1.408(12)	Ring 1 is planar. Ring 2 is bent along line joining C_1 to C_4. See Figure V-A-5.
			C_2-C_3:	1.421(12)	
			C_3-C_4:	1.361(12)	
			C_4-C_5:	1.399(12)	
			C_5-C_6:	1.417(12)	
			C_6-C_1:	1.453(12)	
	$M-R_2^a$:	1.73	C_1-C_2:	1.415(12)	
			C_2-C_3:	1.408(12)	
			C_3-C_4:	1.480(12)	

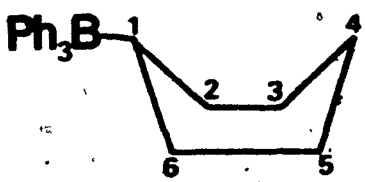


TABLE V-A-1 (CONT'D)

C_4-C_5:	1.498(12)	
C_5-C_6:	1.327(12)	294
C_6-C_1:	1.487(12)	

[a] Represents the distance from the least squares plane of the ring to the metal atom.

[b] The number in parentheses indicates the estimated standard deviation in the last two digits quoted in the length.

by ligand exchange reactions. Indeed, the first report in the literature of the synthesis of benzenetricarbonylchromium(0)[312] involved the reaction of dibenzenechromium(0) with hexacarbonylchromium(0) as illustrated in Equation V-A-3. The arene substitutes for three adjacent carbonyl ligands in the octahedral hexacarbonylchromium(0).

$$(C_6H_6)_2Cr + Cr(CO)_6 \rightarrow 2(C_6H_6)Cr(CO)_3 \qquad \text{V-A-3}$$

A microwave study of benzenetricarbonylchromium(0)[313] indicated the molecule to be a symmetrical top. Local C_{3v} symmetry for the benzenoid moiety would give rise to the model proposed for the bis-arene complexes (*vide supra*). This model was advocated in an infrared study by Fritz and Manchot.[314] The study involved experimental spectra of $(C_6H_6)Cr(CO)_3$ and $(C_6D_6)Cr(CO)_3$ and their comparison to the theoretically-calculated benzenoid local C_{6v} symmetry. There was a lack of fit and a model involving a fixed Kékulé structure for the benzene moiety was proposed.

Infrared studies have also appeared which compare the frequencies of the uncomplexed aromatic hydrocarbons with their corresponding tricarbonylchromium analogs.[315] It is found that the carbon-hydrogen stretching peaks merge into one band, the skeletal carbon-carbon stretching modes shift to lower energy and the carbon-hydrogen out-of-plane vibrations, characteristic of substitution patterns, vanish.

Nuclear magnetic resonance studies of benzenetricarbonylchromium(0)[316] show a single line spectrum which does not distinguish between C_{3v} or C_{6v} benzenoid site symmetry in the complex. A *para* disubstituted benzenoid complex would result in different electronic environments about the remaining hydrogen atoms if a 'frozen-out' Kékulé structure were prevalent. Splitting was sufficiently small in 1,4-dimethoxybenzenetricarbonylchromium(0) to exclude a localized bonding scheme and it was concluded that the π electrons were completely delocalized. A recent[317] study of the ^{13}C nmr spectrum of benzene, toluene and *o*-, *m*- and *p*-xylene chromium tricarbonyls was reported.

By observing the behavior of the infrared carbonyl carbon-oxygen stretching frequencies in various substituted benzenetricarbonylchromium(0) complexes, information about the bonding of the arene has been inferred. Several papers in this field have been published by D.A. Brown and co-workers.[318-321] The work is premised on the fact that the substituent on the ring electronically affects the extent of triple bond character of the carbon-oxygen carbonyl bond. The carbonyl stretching frequency decreases with an increase in the dative (full metal d-orbital to empty benzenoid molecular orbital) back-bonding.

Because electronic charge is being put back into the aromatic system by the synergistic bonding scheme (outlined in the section of this introduction on the bis-arene complexes), the metal is acting as an electron sink with respect to the metal-carbon (carbonyl) bond. This has the effect of removing electronic charge from the carbon-oxygen bond, thus decreasing its strength and, consequently, its infrared stretching frequency.

Although one might be tempted to place a rather quantitative interpretation on this effect, Brown offers a word of caution.[321] Even though there is ample evidence for transmission of electronic effects through the metal atom, it must be appreciated that frequency effects are rarely due to only one bond. Complex molecular vibrations make it necessary to do a complete normal co-ordinate analysis to isolate the effects of each bond.

Such an analysis was accomplished quite recently on benzenetricarbonylchromium(0) by Schäfer *et al.*[322,323] The results, when compared with the experimentally-determined spectra, seem to preclude the possibility of a C_{3v} distortion of the benzene moiety and argue in favour of a fully-delocalized bonding scheme.

The π electron charge used in bonding to the chromium atom decreases the resonance energy of the aromatic moiety thus making it more susceptible to nucleophilic attack than it is in the free state.[324] There is also a considerable involvement of the ring σ orbitals in the ring-to-metal bonding as shown by semiempirical molecular orbital calculations on arene chromium tricarbonyls as reported by Carroll and McGlynn.[325] The importance of the σ orbitals has also been pointed out by Gubin and Khandkarova.[326]

Excellent reviews exist on the bonding, reactions and properties of these 'half-sandwich' complexes.[222,235] It will be instructive to review here the various structure determinations of these arene chromium tricarbonyls and some related complexes. Such a review does not exist at the present time.

In 1959, Corradini and Allegra published the results of a two-dimensional X-ray crystallographic structure investigation on benzenetricarbonylchromium(0).[327–329] The mean carbon-carbon bond length of the arene was found to be 1.401Å although the large standard deviations precluded any discussion of possible bonding abnormalities. It was up to Bailey and Dahl[330] to complete a three-dimensional single crystal X-ray analysis on this complex. Complete anisotropic refinement to a weighted residual index of 4.1% resulted in an accurate structure with highly acceptable standard deviations.

There is no indication of threefold distortion. The molecule lies on the mirror plane of space group $P2_1/m$. The plane goes through the chromium atom and one carbonyl. It relates the two other carbonyls and three of the ring carbons to the other three. There are thus but four crystallographically-independent carbon-carbon bond lengths: 1.371(11), 1.402(08), 1.404(08), and 1.421(11)Å.

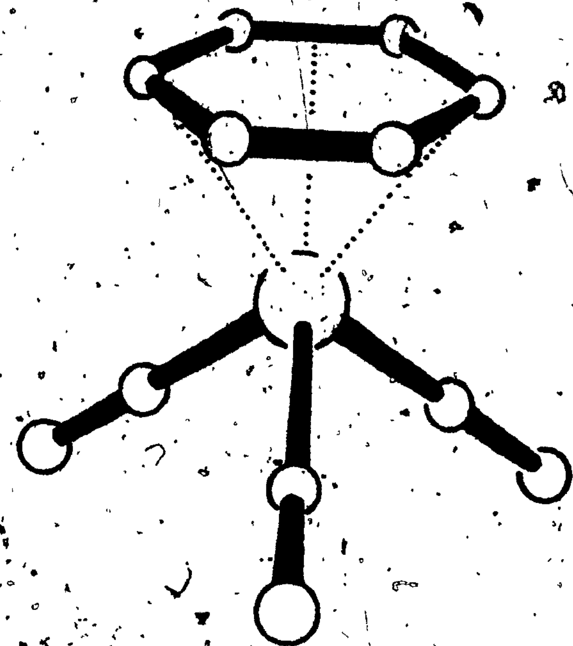
The average chromium-to-arene carbon distance is 2.22Å, somewhat longer than the corresponding distance in dibenzenechromium(0) (2.14Å).[269] In point of fact, the perpendicular distance from the chromium atom to the least squares plane of the aromatic ring is 0.12Å longer in the benzenetricarbonylchromium(0) complex than in dibenzenechromium(0). This is not unreasonable in view of the fact that the carbonyl groups are strong π bonding ligands. This would tend to decrease the extent of chromium-to-benzene back-bonding and thus lengthen the bonding distance in comparison to dibenzenechromium(0).

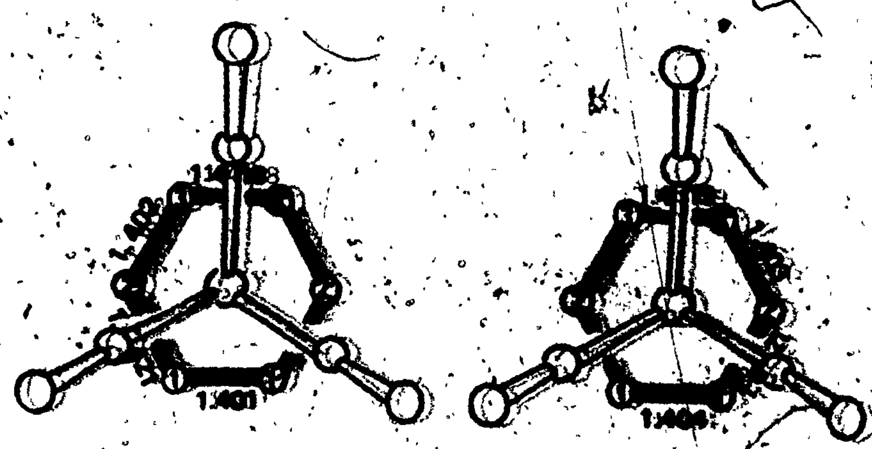
Figure V-A-7a illustrates the structure of benzenetricarbonylchromium(0) as found by Allegra and Dahl. The plane of the three carbonyl carbons is parallel to that of the benzene moiety. Extension of the oxygen-carbon carbonyl vectors results in their intersection with the midpoint of alternate carbon-carbon bonds in the benzene moiety.

Figure V-A-7a. The structure of benzenetricarbonyl-chromium(0).

Figure V-A-7b. Bond lengths in benzene-tricarbonylchromium(0) as determined by X-ray diffraction.

Figure V-A-7c. Bond lengths in benzene-tricarbonylchromium(0) as determined by neutron diffraction.




1.401

In order to investigate the somewhat tempting hypothesis that the benzenoid ring has full sixfold symmetry, Dahl undertook a rigid body least squares refinement of the data. Here, the benzene ring was constrained to have D_{6h} symmetry with a uniform C-C bond length of 1.392Å and a carbon-hydrogen bond length of 1.08Å. The weighted discrepancy factor for this isotropic refinement was compared to that for the C_s data using Hamilton's R factor test.[267] The two models were not found to be statistically equivalent $\{R_{wf}(D_{6h})/R_{wf}(C_s) = 1.021\}$ although, within three standard deviations, the irregular deviations of bond lengths in the ring can be ignored in favour of the more symmetrical structure.

Recently the preliminary report of an independent X-ray study on benzenetricarbonylchromium(0) including a neutron diffraction study has been published.[331] Although the X-ray structure work of Bailey and Dahl appeared rather definitive, a low temperature (78°K) data collection by both X-ray and neutron diffraction methods gave mutually compatible results not in agreement with the room temperature study.

Rees and Coppens[311] do, in fact, report an alteration in the C-C bond lengths of the benzene ring. The average 'short' bond is 1.401(1)Å by neutron diffraction whereas the corresponding average 'long' bond is 1.419(1)Å and 1.420(2)Å respectively. The difference is about

0.017(2)Å, well beyond three standard deviations and thus statistically significant. The fact that the two independent studies agree lends further credence to a localized bonding scheme. We shall now examine the ramifications of the findings of these authors.

Figure V-A-7b gives a representation of the geometry of benzenetricarbonylchromium(0) as found by X-ray diffraction by Rees and Coppens. The view is down the *pseudo*threefold axis which contains the chromium atom. The crystallographic mirror plane is parallel to the projection direction. Figure V-A-7c shows the molecular geometry as determined by neutron diffraction. Hydrogen atoms have been excluded from these diagrams to increase clarity. A cursory observation will show that the results are compatible within experimental error.

In order for the chromium atom to have an octahedral co-ordination, the localized bonds to the benzene must be extensions of the carbonyl-chromium vectors. This means that, in a Kékulé type bonding scheme, the olefinic C1-C1', C2-C3 and C2'-C3' bonds are involved in co-ordination to the metal. This is contrary to what would be expected based on the bond lengths reported. Indeed, the bonds involved in octahedral co-ordination are the shortest whereas one would expect, based on the evidence from many studies on three-centered olefinic and acetylenic bonded complexes, a lengthening of the C-C distance. The authors submit that the longest bonds may well be involved thus making the co-ordination about the chromium trigonal prismatic.

Bailey and Dahl[332] have also published the X-ray crystallographic structure determination of hexamethylbenzenetricarbonylchromium(0). With 1447 independent planes, the Pbca structure converged at an anisotropic discrepancy factor of 10.5%. The mean C-C arene distance was 1.417Å although a twofold distortion seemed to be present. This cannot be due to twofold molecular disorder as it is for the dibenzenechromium(0) complex described before. To test this possibility (of twofold distortion), the ring was refined as a rigid body (D_{6h}) isotropically and the converged weighted reliability index was compared with its converged isotropic analog without D_{6h} imposed symmetry. Hamilton's *R* factor test showed that the D_{6h} model was not preferred.

Commenting on the twofold distortion, Dahl claims that the free ligand, hexamethylbenzene, is twofold distorted. This distortion is due to steric effects of the methyl groups which are in close proximity according to the authors. A two-dimensional X-ray structure analysis, albeit conducted over forty years ago, by Lonsdale[333] indicated no such distortion. The distance from the chromium atom to the least squares plane of the hexamethylbenzene ring in hexamethylbenzenetricarbonylchromium(0) is 1.73Å, in harmony with the value of 1.72Å found for benzenetricarbonylchromium(0).[330]

The complex biphenyl-bis(tricarbonylchromium(0)) has been synthesized and a two-dimensional X-ray crystallographic structure determination has been reported.[334,335] One chromium tricarbonyl moiety is bonded in the same way as benzenetricarbonylchromium(0) to one ring in biphenyl whereas the other tripod is bonded similarly to the second ring but on the opposite side. The complex thus possesses an inversion center midpoint along the bond joining the two phenyl rings.

The two-dimensional X-ray diffraction structure determination of phenanthrenetricarbonylchromium(0) was undertaken to discover whether the chromium tricarbonyl tripod bonds to the central ring or to an outer ring. The outer ring is preferred[336] in this monoclinic form studied although the structure determination was far from accurate. With 504 reflections in space group $P2_1/a$, refinement gave a reliability index of 13%. The extended carbonyl chromium vectors cut the three alternate carbon-carbon bonds which include that of ring fusion.

Phenanthrenetricarbonylchromium(0) also crystallizes in space group Pbca. Muir, Ferguson and

Sim[337,338] found, in a three-dimensional single crystal X-ray crystallographic study, that the ring electrons are not appreciably localized in these complexes. From anisotropic refinement of 4169 independent planes to an *R* factor of 12%, the authors quote a mean C-C distance of 1.412Å in the bonded ring and contrast this with a mean bond length of 1.396Å in the other rings which do not bond to the $Cr(CO)_3$ fragment. Some anomalies exist in the metal-to-carbon distances which bear some consideration.

The chromium-carbon distances to the four carbons which are hydrogen substituted are 2.212(5), 2.210(5), 2.206(5) and 2.208(4)Å with a mean of 2.209Å. However, the chromium-carbon distance for the other two carbons of the ring (those fused to the rest of the aromatic moiety) are 2.289(4) and 2.289(4)Å. This suggests that the latter two bonds are less than unity and implies that those carbons are less capable of forming bonds to chromium than the other four. The 2.209Å bonds are considered to have unitary bond order based on the sum of the chromium(0) atomic radius of 1.48Å[339] and that of an sp^2 carbon atom (0.74Å). Perhaps, in this complex, there are then less than six electrons involved in metal-to-arene π bonding.

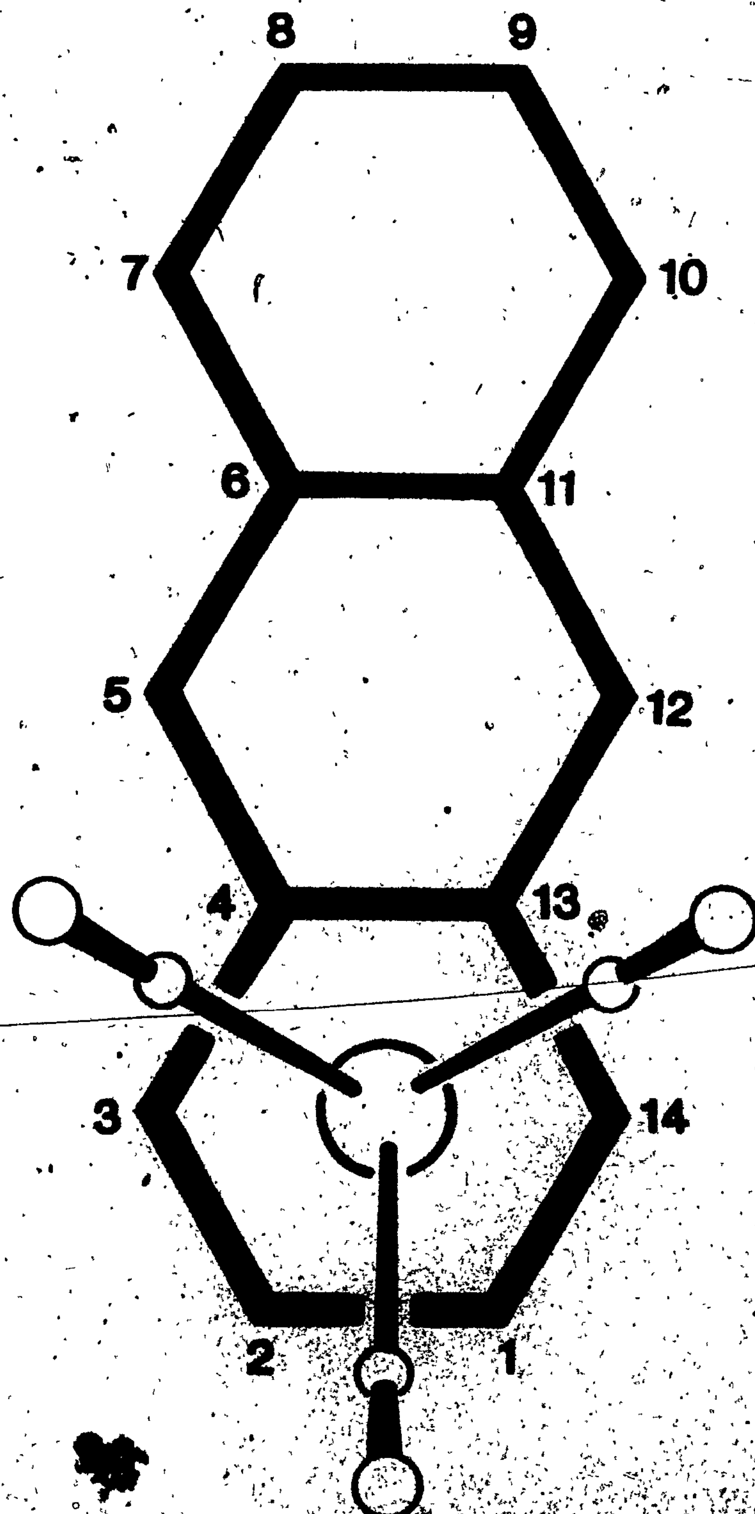
A very similar bonding pattern is observed for the complex anthracenetricarbonylchromium(0).[340,341] Free anthracene shows unequal alternating C-C distances of

1.388Å and 1.430Å in each of the outer rings.[342] In the transition metal complex, the mean alternate carbon-carbon distances in the outer nonbonded ring are similar to the free anthracene at 1.390Å for C_7-C_8, C_9-C_{10} and C_{11}-C_6 and for C_6-C_7, C_8-C_9 and C_{10}-C_{11} (see Figure V-A-8 for a description of the numbering scheme used). The effect of the bonded chromium tricarbonyl on the outer ring is to cause equalization of these alternate bond lengths (mean of C_3-C_2, C_1-C_{14}, C_{13}-C_4 is 1.414Å and mean of C_4-C_3, C_2-C_1, C_{14}-C_{13} is 1.423Å). The overall effect is to lengthen those bonds that would be involved in an octahedral localized bonding scheme. This effect is in marked contrast to that observed by Rees and Coppens [331] for benzenetricarbonylchromium(0).

Crystallographic X-ray structure determinations have also been accomplished on naphthalenetricarbonylchromium(0)[343] ~~and~~ α-aminonaphthalenetricarbonylchromium(0).[344] The metal bonds to the unsubstituted ring in the latter complex with the same lengthening of the chromium fused-ring carbons as observed for the orthorhombic phenanthrene complex.[338] The six C-C bonds show no evidence of localized bonding however.

Muir and Ferguson have published[345] the structure of 9,10-dihydrophenanthrenetricarbonylchromium(0) which crystallizes in space group $P2_1/c$. The same effect

Figure V-A-8. Anthracenetricarbonylchromium(0). The numbering scheme is as in the original reference.


8
9
7
10
6
11
5
12
4
13
3
14
2
1

(the two anomalous chromium-carbon distances) as with the phenanthrene analog is seen here but the difference in the lengths is not as great (2.206(4) and 2.400(4)Å). All pertinent information on the geometries of these complexes can be found in Table V-A-2.

b) Substituted Arene Chromium Tricarbonyls

In all the complexes discussed above, the projection of the carbonyl ligands onto the plane of the six-membered ring intersects alternate C-C bonds. There are complexes, however, in which the carbonyls lie directly over every second carbon atom in the arene. We shall now examine what factors determine why this should occur.

G.A. Sim and co-workers at the University of Sussex as well as Dusausoy and Protas at Nancy, France, have been largely responsible for the X-ray diffraction studies of substituted arene chromium tricarbonyls. These researchers have placed groups on benzene which affect the ring electronically and have complexed these rings to chromium tricarbonyl. Structure analyses have exposed trends in these compounds for which rationalizations have been proposed.

TABLE V-A-2

INTERATOMIC DISTANCES IN SOME ARENE-CHROMIUM TRICARBONYLS[b]

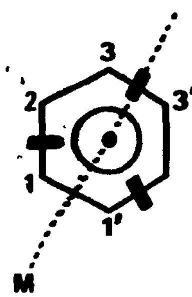
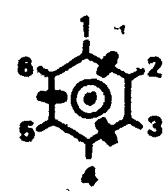
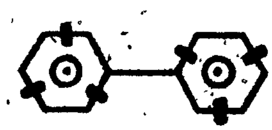
COMPOUND	METAL-ARENE DISTANCE (Å)		ARENE CARBON-CARBON DISTANCES (Å)		REMARKS AND REFERENCE
Benzene-	$M-C_1$:	2.230(09)	$C_1-C_{1'}$:	1.371(11)	Bailey
tricarbonyl-	$M-C_2$:	2.218(08)	C_1-C_2:	1.402(08)	and Dahl
chromium(0)	$M-C_3$:	2.216(08)	C_2-C_3:	1.404(08)	330
	$M-R$[a] :	1.72_4	$C_3-C_{3'}$:	1.421(11)	
	$M-C_1$:	2.240(02)	$C_1-C_{1'}$:	1.401(02)	X-ray
	$M-C_2$:	2.229(02)	C_1-C_2:	1.421(02)	data
	$M-C_3$:	2.217(02)	C_2-C_3:	1.402(02)	78°K
			$C_3-C_{3'}$:	1.418(02)	331
	$M-C_1$:	2.240(03)	$C_1-C_{1'}$:	1.404(02)	Neutron
	$M-C_2$:	2.230(03)	C_1-C_2:	1.420(02)	Diffract.
	$M-C_3$:	2.220(03)	C_2-C_3:	1.403(02)	78°K
			$C_3-C_{3'}$:	1.419(03)	331
Hexamethyl-	$M-C_1$:	2.211(09)	C_1-C_2:	1.448(13)	
benzene-	$M-C_2$:	2.253(10)	C_2-C_3:	1.461(14)	
tricarbonyl-	$M-C_3$:	2.235(10)	C_3-C_4:	1.379(14)	
chromium(0)	$M-C_4$:	2.226(11)	C_4-C_5:	1.419(14)	
	$M-C_5$:	2.241(09)	C_5-C_6:	1.424(13)	
	$M-C_6$:	2.233(11)	C_6-C_1:	1.370(13)	332
Diphenyl-	$M-C_x$:	Average	C_x-C_y:	Not reported	
bis-(tricarbonyl-		2.20 ± 0.03			
chromium(0))					334

TABLE V-A-2 (CONT'D)

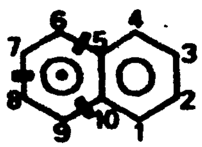
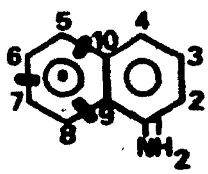
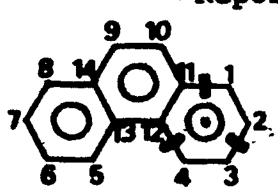
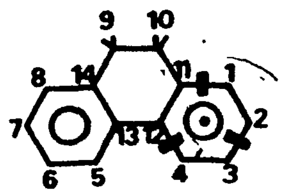
Naphthalene-	$M-C_9$: 2.214	C_9-C_8 : 1.38(02)	E.s.d.
tricarbonyl-	$M-C_8$: 2.213	C_8-C_7 : 1.38(02)	not quoted
chromium(0)	$M-C_7$: 2.191	C_6-C_7 : 1.39(02)	for the
	$M-C_6$: 2.186	C_6-C_5 : 1.40(02)	metal-
	$M-C_5$: 2.306	C_5-C_{10}: 1.44(02)	carbon
	$M-C_{10}$: 2.337	$C_{10}-C_9$: 1.45(02)	distances
			343
1-amino-	$M-C_8$: 2.19(02)	C_8-C_7 : 1.43(03)	
naphthalene-	$M-C_7$: 2.23(02)	C_7-C_6 : 1.41(03)	
tricarbonyl-	$M-C_6$: 2.24(02)	C_6-C_5 : 1.43(03)	344
chromium(0)	$M-C_5$: 2.22(02)	C_5-C_{10}: 1.42(03)	
	$M-C_{10}$: 2.30(02)	$C_{10}-C_9$: 1.43(03)	
	$M-C_9$: 2.30(02)	C_9-C_8 : 1.45(03)	
Anthracene-	$M-C_{14}$: 2.219(08)	$C_{14}-C_1$:1.372(13)	See
tricarbonyl-	$M-C_1$: 2.217(09)	C_1-C_2 :1.416(14)	Figure
chromium(0)	$M-C_2$: 2.221(09)	C_2-C_3 :1.420(14)	V-A-8.
	$M-C_3$: 2.215(09)	C_3-C_4 :1.442(12)	341
	$M-C_4$: 2.340(08)	C_4-C_{13}:1.449(12)	
	$M-C_{13}$: 2.234(08)	$C_{13}-C_{14}$:1.410(11)	
Phenanthrene-	$M-C_x$: Not	C_1-C_2 : 1.37(09)	Monoclinic
tricarbonyl-	Reported	C_2-C_3 : 1.40(09)	form.
chromium(0)		C_3-C_4 : 1.54(09)	336
		C_4-C_{12}: 1.36(09)	
		$C_{12}-C_{11}$: 1.37(09)	
		$C_{11}-C_1$: 1.56(09)	
	$M-C_1$: 2.212(05)	C_1-C_2 :1.389(07)	Ortho-
	$M-C_2$: 2.210(05)	C_2-C_3 :1.385(07)	rhombic
	$M-C_3$: 2.206(05)	C_3-C_4 :1.410(06)	form.
	$M-C_4$: 2.208(04)	C_4-C_{12}:1.439(06)	338
	$M-C_{12}$: 2.289(04)	$C_{12}-C_{11}$:1.410(06)	
	$M-C_{11}$: 2.289(04)	$C_{11}-C_1$:1.440(06)	

TABLE V-A-2 (CONT'D)

9,10-dihydro-phenanthrene-tricarbonyl-chromium(0)	M-C_1 :	2.209(04)	C_1 -C_2 :	1.383(06)	345
	M-C_2 :	2.208(04)	C_2 -C_3 :	1.392(07)	
	M-C_3 :	2.207(04)	C_3 -C_4 :	1.400(06)	
	M-C_4 :	2.200(04)	C_4 -C_{12}:	1.415(06)	
	M-C_{12}:	2.248(03)	C_{12}-C_{11}:	1.407(05)	
	M-C_{11}:	2.232(04)	C_{11}-C_1 :	1.422(06)	



a Represents the distance from the least squares plane of the ring to the metal atom.

b The heavy lines shown in the rings in the illustrations are projections of the carbonyl vectors onto the plane of the ring. The number in parentheses indicates the estimated standard deviation in the last two digits quoted in the length.

Carter, McPhail and Sim[346] studied the X-ray diffraction analysis of methylbenzoatetricarbonylchromium(0). The authors found that, for octahedral co-ordination about the chromium atom, the extension of the carbonyl-chromium vectors implied bonding, not to the closest point which is midway between two carbons, but to carbon atoms carrying the greatest amount of negative charge. Through the mesomeric effect of the carbomethoxy group, electronic charge is removed in favour of relative electron excess in the *meta* positions.

The same effect has been observed for *o*-hydroxyacetylbenzenetricarbonylchromium(0) and the *o*-methoxyacetylbenzene analog.[347-349] The former complex crystallizes in space group $P2_12_12_1$. With 410 reflections, the anisotropic refinement to 8.7% revealed no systematic differences in the bonding of chromium to ring carbons. There is a hydrogen bonded interaction between the acetyl oxygen and the hydrogen of the hydroxy group. All the substitutent atoms are in the plane of the benzene ring.

Such is not the case for the methoxy derivative. The carbonyl oxygen is positioned above the plane of the benzene ring, the methyl group of the acetyl being consequently closer to the chromium tricarbonyl tripod. The angle between the planes of the acetyl group and the benzene plane is 21°. The methoxy methyl group is also positioned below the benzene ring plane closer to the chromium tricarbonyl moiety. *O*-methoxyacetylbenzenetricarbonylchromium(0) crystallizes in space group $Pna2_1$ and 450 independent planes give an anisotropic refinement discrepancy factor of 7.6%. Again no systematic bond length differences can be detected.

In both these complexes, the acetyl group, through the mesomeric effect, enhances the relative electron density at positions in the ring *meta* to itself and in the substituted carbon atom. The inductive effect of the other substituent (hydroxy or methoxy) is to enhance electron density *ortho* and *para* to it. Since these complexes are *ortho* substituted, this inductive effect is reinforcing and the electron density at positions 1,3 and 5 is quite high relative to that at positions 2, 4 and 6. These two complexes exist as enantiomers and studies have been made on these and other similar chiral complexes.[350]

Inasmuch as *meta*-directing acetyl groups force a preferred conformation of the chromium tricarbonyl tripod, so do *ortho*-and *para*-directing substituents. Sim *et al.*[351,352] have reported the structure of 2-methylanilinetricarbonylchromium(0) in which the amine, acting as an *ortho-para*-directing group, is responsible for the direction of the localized σ orbitals of the chromium atom. Since the methyl group is also electron releasing, one might have expected a conflict but the amine function has a much more negative σ effect than the methyl group.

Methoxy is also *ortho-para*-directing and thus the same behavior would be expected for methoxybenzenetricarbonylchromium(0) as was seen for the amine complex. This was indeed found to be true for this complex[353] and for its 1,3,5-trinitrobenzene charge transfer analog whose crystal structure was also reported.[354]

Bush, Dullforce and Sim [355] have reported the absolute configuration of (+)-tricarbonylchromium-*o*-toluic acid and (-)-tricarbonylchromium-*m*-toluic acid. A staggered conformation (similar to benzenetricarbonylchromium(0)) was found for these two complexes. The lack of electron density preference on the ring may be due to the fact that the mesomeric effect of the carboxy group enhances the charge in the *ortho* and *para* positions with respect to the *meta* positions by removing charge from the ring. The inductive effect acts in an opposite sense to replace this charge through the σ system.

Even more confusing is the discovery by the Dusausoy-Protas group [356] that the acetylbenzenetricarbonylchromium(0) complex is in the staggered rather than in the eclipsed conformation. The effect of the acetyl group should be to cause *meta*-direction of the electron charge (*viz.* the methylbenzoatetricarbonylchromium(0) complex[346]) and thus an eclipsed conformation. Crystal packing forces may be responsible for this anomoly because in solution the two complexes behave identically.[357]

Three other arene chromium tricarbonyl complexes are worthy of mention here. The crystal and molecular structures of π-(*exo*-2-acetoxybenzonorbornenyl)-*exo*-tricarbonylchromium(0) has been reported.[358] The chromium tricarbonyl tripod is bonded in the staggered conformation to the benzo-portion of the molecule. The chromium-to-least squares plane of the ring distance is normal and the C-C distances in the arene show no anomaly. The staggered position of the tripod is not viewed here as resulting from any electronic effects but is due primarily to the steric interaction with the hydrogen on the *exo*-norbornadiene bridgehead carbon.

Bowden and Colton[359] have reported the isolation of chromium, molybdenum and tungsten tricarbonyl tris-(2-methylphenyl)phosphines in which one of the three 2-methylphenyl groups is π bonded to the metal. Colton *et al.*[360] have also reported the isolation of a chromium bis(diphenylarsino)methane complex in which one arsenic atom is σ bonded to a chromium dicarbonyl fragment which π bonds to a phenyl ring on the other arsenic. This molecule has been studied by X-ray diffraction and for 3213 independent planes in the centrosymmetric triclinic space group, an anisotropic reliability index of 9.0% was obtained.[361] The molecule is described in Figure V-A-9. No unusual bond lengths are observed.

All the foregoing chromium tricarbonyl substituted arene complexes which have been subjected to X-ray crystallographic structure analysis are listed in Table V-A-3 along with important quoted bond lengths. The projections of the carbonyl-chromium vectors onto the plane of the ring are marked by solid lines to illustrate the staggered or eclipsed conformations.

c) Other Transition Metal Carbonyl Arene Complexes

In 1969, Snow *et al.*[362] reported the structure of the hexamethylbenzeneiodotricarbonyltungsten(I) cation as its triiodide salt. The projections of the inorganic ligand-tungsten vectors onto the plane of the hexamethylbenzene ring must perforce be partly staggered and partly eclipsed. The bulky iodine atom lies under the midpoint of an arene C-C bond.

Various vanadium π-arene complexes have been

Figure V-A-9. Molecular configuration of the complex $Ph(\pi\text{-}Ph)As\cdot CH_2\cdot AsPh_2Cr(CO)_2$

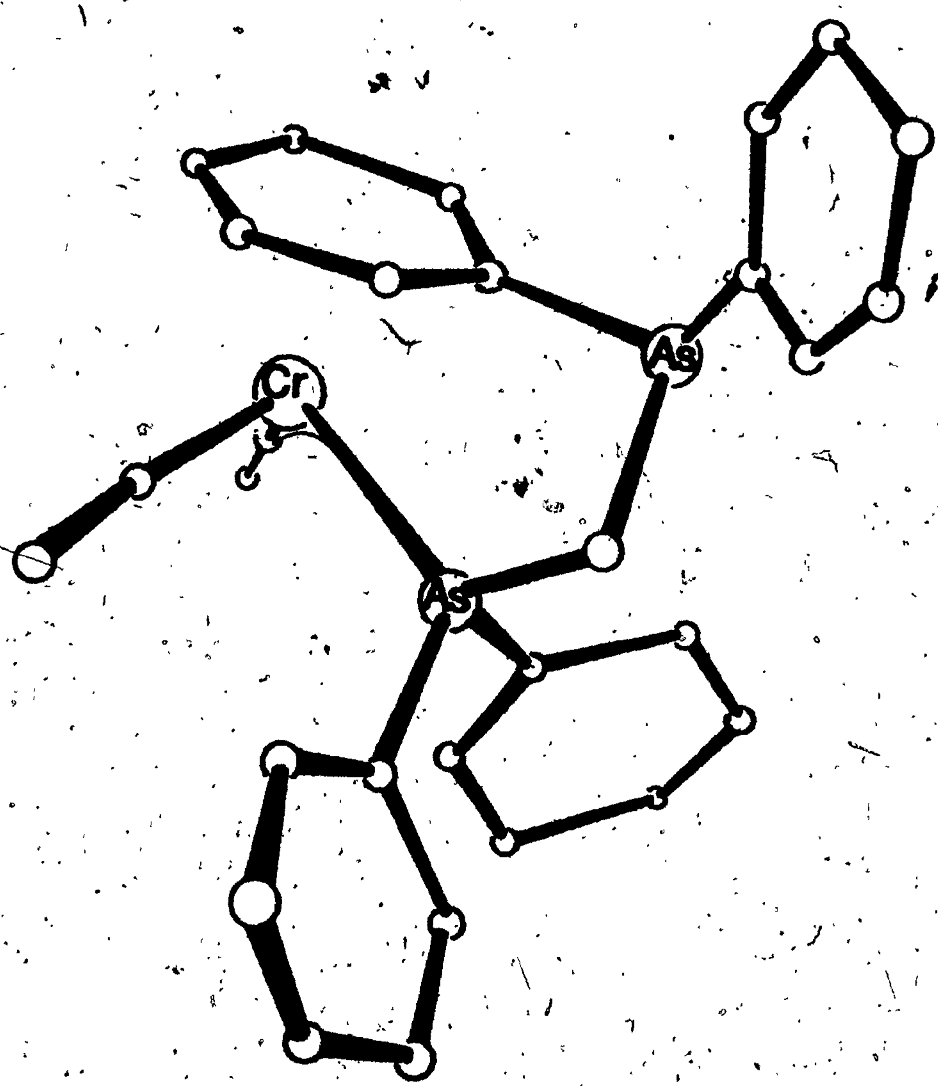

Cr
As
As

TABLE V-A-3

INTERATOMIC DISTANCES IN SOME SUBSTITUTED ARENE CHROMIUM TRICARBONYL COMPLEXES[a]

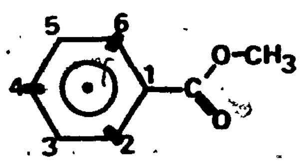
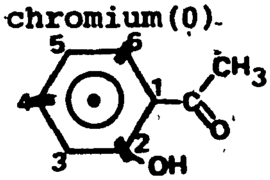
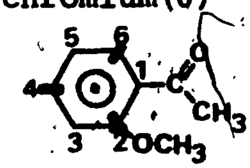
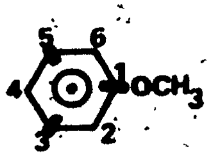
COMPOUND	METAL-ARENE DISTANCE (Å)		ARENE CARBON-CARBON DISTANCES (Å)		REMARKS AND REFERENCE
Methylbenzoate-	$M-C_1$:	2.21(1)	C_1-C_2:	1.42(1)	346
tricarbonyl-	$M-C_2$:	2.21(1)	C_2-C_3:	1.39(2)	
chromium(0)	$M-C_3$:	2.21(1)	C_3-C_4:	1.43(2)	
	$M-C_4$:	2.25(1)	C_4-C_5:	1.40(2)	
	$M-C_5$:	2.22(1)	C_5-C_6:	1.45(1)	
	$M-C_6$:	2.20(1)	C_6-C_1:	1.40(1)	
O-hydroxyacetyl-	$M-C_1$:	2.16(2)	C_1-C_2:	1.49(4)	349
benzenetri-	$M-C_2$:	2.33(3)	C_2-C_3:	1.46(5)	
carbonyl-	$M-C_3$:	2.30(3)	C_3-C_4:	1.41(5)	
chromium(0)	$M-C_4$:	2.27(4)	C_4-C_5:	1.42(5)	
	$M-C_5$:	2.26(3)	C_5-C_6:	1.44(5)	
	$M-C_6$:	2.16(2)	C_6-C_1:	1.42(4)	
O-methoxyacetyl-	$M-C_1$:	2.24(2)	C_1-C_2:	1.47(4)	349
benzenetri-	$M-C_2$:	2.28(3)	C_2-C_3:	1.49(3)	
carbonyl-	$M-C_3$:	2.26(3)	C_3-C_4:	1.34(4)	
chromium(0)	$M-C_4$:	2.22(3)	C_4-C_5:	1.49(4)	
	$M-C_5$:	2.20(2)	C_5-C_6:	1.35(4)	
	$M-C_6$:	2.20(2)	C_6-C_1:	1.40(4)	
Anisole-	$M-C_1$:	2.25	C_1-C_2:	1.38(2)	E.s.d.
tricarbonyl-	$M-C_2$:	2.20	C_2-C_3:	1.43(2)	not quoted
chromium(0)	$M-C_3$:	2.22	C_3-C_4:	1.39(2)	for metal
	$M-C_4$:	2.22	C_4-C_5:	1.39(2)	to carbon
	$M-C_5$:	2.25	C_5-C_6:	1.42(2)	distance.
	$M-C_6$:	2.27	C_6-C_1:	1.44(2)	353

TABLE V-A-3 (CONT'D)

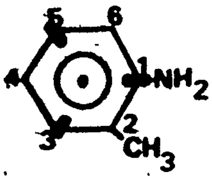
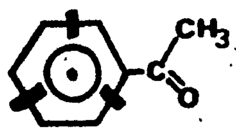
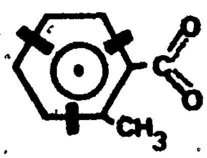
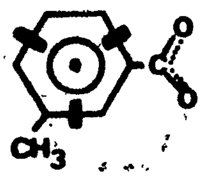
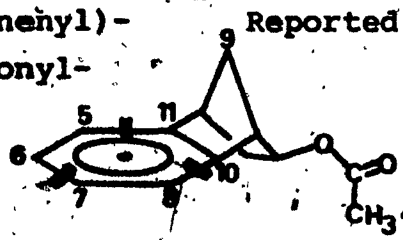
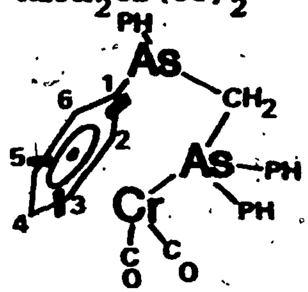
Toluidene-tricarbonyl-chromium(0) 	$M-C_1$: 2.37(1) $M-C_2$: 2.26(1) $M-C_3$: 2.20(1) $M-C_4$: 2.23(2) $M-C_5$: 2.23(1) $M-C_6$: 2.23(2)	C_1-C_2: 1.44(2) C_2-C_3: 1.40(2) C_3-C_4: 1.37(2) C_4-C_5: 1.38(2) C_5-C_6: 1.43(2) C_6-C_1: 1.38(2)	352
Acetylbenzene-tricarbonyl-chromium(0) 	$M-C_x$: Not Reported	C_x-C_y: Not Reported	356
(+)-tricarbonyl-chromium-*o*-toluic acid 	$M-C_x$: Average 2.21 ± 0.00[6]	C_x-C_y: Not Reported	355
(−)-tricarbonyl-chromium-*m*-toluic acid 	$M-C_x$: Average 2.20 ± 0.00[4]	C_x-C_y: Not Reported	355
π-(*exo*-2-acetoxy-benzonorbornenyl)-*exo*-tricarbonyl-chromium(0) 	$M-C_x$: Not Reported	C_8-C_7: 1.46(1) C_7-C_6: 1.44(1) C_6-C_5: 1.47(1) C_5-C_{11}: 1.42(1) $C_{11}-C_{10}$: 1.41(1) $C_{10}-C_8$: 1.43(1)	358

TABLE V-A-3 (CONT'D)

Ph(π-Ph)As·CH_2·$AsPh_2Cr(CO)_2$ 	$M-C_1$:	2.18(2)	C_1-C_2:	1.45(2)	361
	$M-C_2$:	2.22(2)	C_2-C_3:	1.45(2)	
	$M-C_3$:	2.20(2)	C_3-C_4:	1.37(2)	
	$M-C_4$:	2.18(2)	C_4-C_5:	1.38(2)	
	$M-C_5$:	2.19(2)	C_5-C_6:	1.47(2)	
	$M-C_6$:	2.22(2)	C_6-C_1:	1.40(2)	

[a] The dark lines in the rings are the projections of the carbonyl vectors onto the plane of the ring.

reportedly synthesized[363,364] although none have been investigated by X-ray diffraction. Hexacarbonylvanadium(0) reacts with arenes with valence disproportionation to give arenetetracarbonylvanadium(I) vanadiumhexacarbonyl(-I) salts. The yields of the ionic complexes are as follows: naphthalene (<1%), anisole (<1%), *o*-xylene (29.8%), 1,2,4-trimethylbenzene (32.1%), 1,3,5-trimethylbenzene (40.9%) and 1,2,3-trimethylbenzene (53.4%). Calderazzo[365] claims that the increase in percentage yield parallels the increased resistance against ligand elimination with increased methyl substitution.

In 1967, Lewis *et al.* reported the preparation of a ruthenium cluster $Ru_6C(CO)_{17}$ and an arene derivative $Ru_6C(CO)_{14}$(arene) in which the arene is either toluene, xylene or mesitylene.[366] The two products were obtained by refluxing $Ru_3(CO)_{12}$ with the appropriate arene and chromatographing the products. This is the first example of a π bonded arene cluster complex. The red cluster $Ru_6C(CO)_{17}$ was obtained in 5% yield whereas the purple complex in which an arene substitutes for three carbonyls on one ruthenium atom was obtained in higher yield according to a more complete report of the synthesis and nmr studies of these complexes.[367]

In 1968, Mason and Robinson[368] completed the X-ray diffraction study of the mesitylene cluster. The complex crystallizes in space group $P2_1/m$ and isotropic refinement to a discrepancy factor of 8.4% for 1195 reflections has resulted in estimated standard deviations of 0.007Å for ruthenium-ruthenium bonds, 0.04Å for ruthenium-carbon bonds and 0.06Å for carbonyl carbon-oxygen bonds. The ruthenium atoms form a slightly distorted octahedron with a carbon atom at its center. All four ruthenium atoms are eight co-ordinate. Three metal atoms (forming a triangular face of the octahedron) are each bonded to four other metal atoms, the carbon and three terminal carbonyl ligands. Two other ruthenium atoms are each likewise bonded to four metal atoms and the carbon but they are bonded to but two terminal carbonyls, being bridged by a third carbonyl. The last ruthenium is bonded to four metal atoms, the carbon and the mesitylene moiety which acts as a six electron donor.

The mean ruthenium-carbon(arene) distance is 2.24Å. There could not have been obvious variations in the ring bond lengths since the authors chose but to quote the mean. The structure is reported for the interest the carbide represents and not to describe the arene-metal bonding. Perhaps a full paper published in time will allow a more critical evaluation of the π-arene bonding scheme in this complex.

Another cluster compound which contains

a π bonded arene ligand has been reported. Penfold and Robinson[108] have very recently published a review on the tricobalt carbon organometallic cluster complexes. In these compounds, a tetrahedron is formed in which three cobalt atoms form the basal plane and a monosubstituted carbon atom is the apex. The first report of these complexes was the preparation of $YCCo_3(CO)_9$ in 1958.[369] Here Y represents halogen, alkyl, aryl or carboxy groupings. To date detailed crystal structures have been reported for thirteen compounds containing the Co_3C cluster.

Reaction of $CH_3CCo_3(CO)_9$ with mesitylene has resulted in the substitution of three carbonyl ligands on one cobalt atom by π mesitylene. This was first reported in 1968 by Robinson, Spencer and Hodges.[109] Nuclear magnetic resonance indicated the presence of the π bonded arene (5.46 δ) and the infrared bands in the carbonyl region were consistent with C_s symmetry for the complex.

The reaction of the cluster with arene is completely reversible and removal of carbon monoxide as the reaction progresses helps increase the yield of the product.[370] Many arenes were used. Hexamethylbenzene, hexafluorobenzene and methylbenzoate do not react with the cluster. Of those arenes that do react, the order of stability of the clusters formed appears, from their ease of formation, to be mesitylene > xylene > toluene > benzene. It was also noticed that the carbonyl stretching frequencies decrease with the increasing electron donating ability of the arene (benzene to mesitylene) as seen in Table V-A-4. According to the synergistic bonding scheme of transition metal carbonyls, the higher electron density from the arene increases the availability of electronic charge for back-bonding with the carbonyl carbon. This extra electronic charge further populates a π^* orbital on the carbon and thus decreases the order of the carbon-oxygen bond. This accounts for the lower infrared stretching frequency observed for the more electron releasing arenes.

A structure determination has been effected on the π-mesitylenephenylmethinylhexacarbonyltricobalt(0) and, first published as a note,[371] it was subsequently reported as a full paper.[372] The crystals are orthorhombic (space group Pnma) with but four molecules in the unit cell. The molecule lies on a crystallographic mirror plane which relates the two halves of both the π bonded mesitylene and the phenyl substituent.

In this cluster compound, the independent cobalt-arene carbon distances are 2.15(2), 2.17(1), 2.09(1) and 2.17(2) Å which gives an average value of 2.15(3) Å. The cobalt atom is 1.61 Å from the center of the mesitylene ring. The C-C arene bond lengths do not vary within standard deviations (1.41(1), 1.42(2), and 1.41(2) Å) giving

TABLE V-A-4

INFRARED SPECTRA OF SOME $PhCCo_3(CO)_6$(ARENE) COMPLEXES $(2200-1700 cm^{-1})$

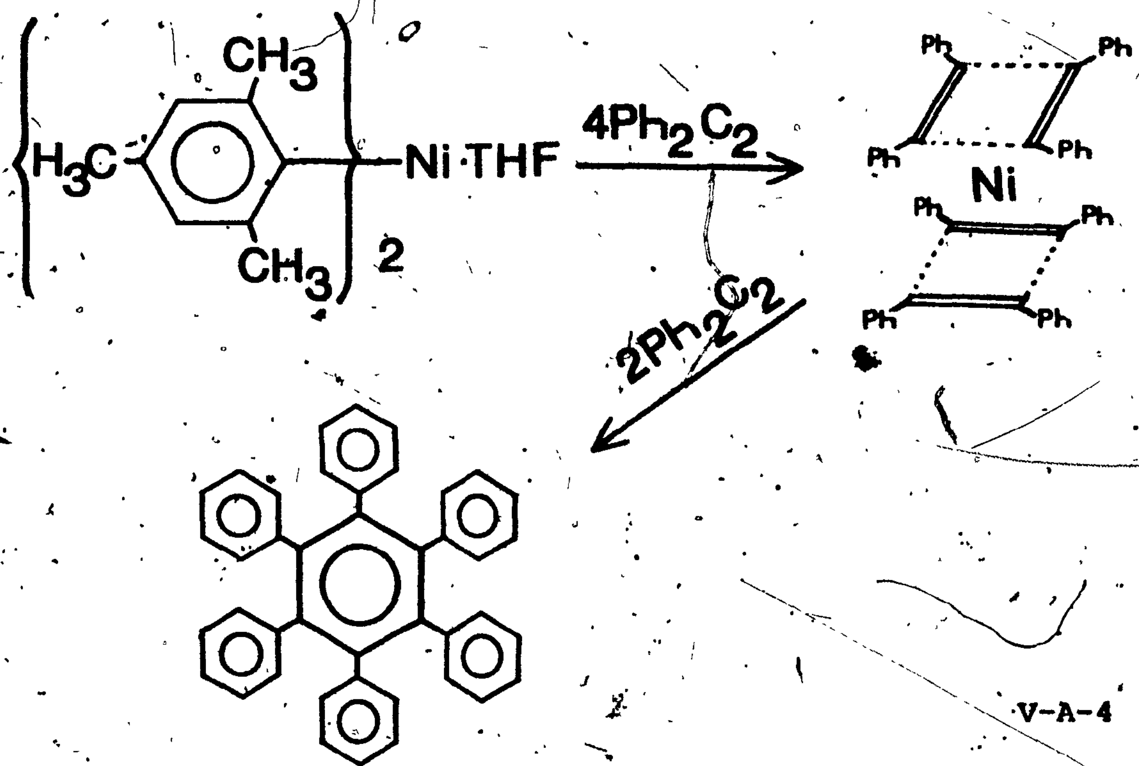
$PhCCo_3(CO)_6$(mesitylene)	2063	2020	2006	1984	1971
$PhCCo_3(CO)_6$(*o*-xylene)	2064	2023	2008	1987	1973
$PhCCo_3(CO)_6$(*m*-xylene)	2064	2023	2008	1986	1973
$PhCCo_3(CO)_6$(*p*-xylene)	2065	2023	2009	1986	1973
$PhCCo_3(CO)_6$(toluene)	2066	2024	2009	1989	1976
$PhCCo_3(CO)_6$(benzene)	2067	2026	2011	1992	1978

a mean value of 1.41(1)Å whereas the mean C-C phenyl distance in the same molecule is 1.37(3)Å. This molecule provides a classical example of the lengthening of the bonds upon complexation with respect to the phenyl bonds. The authors comment on the fact that the arene replaces three carbonyls on one cobalt rather than replacing the three axial carbonyls (one on each of the cobalt atoms) to bond π to all three cobalts as is the case for the π-cyclooctatetraenephenylmethinylhexacarbonyltricobalt(0) complex.[371]

4. Cyclic Trimerization of Acetylene

The field of cyclic trimerization of acetylenes has been recently reviewed.[373] It will be sufficient here to show the connection between π-arene complexes of transition metals and the catalytic synthesis of substituted benzenes from acetylene.

Tsutsui and Zeiss[374] independently from G.N. Schrauzer,[375] showed that dimesitylnickel(II) tetrahydrofuranate reacts with tolane (diphenylacetylene) in a one to four ratio to give an intractable black material which subsequently reacts with two further moles of tolane to give two moles of hexaphenylbenzene (Equation V-A-4). The concept of π bonded acetylene trimerization was extrapolated to chromium, manganese and cobalt systems through the work of Herwig, Zeiss and Tsutsui.[376-378]



V-A-4

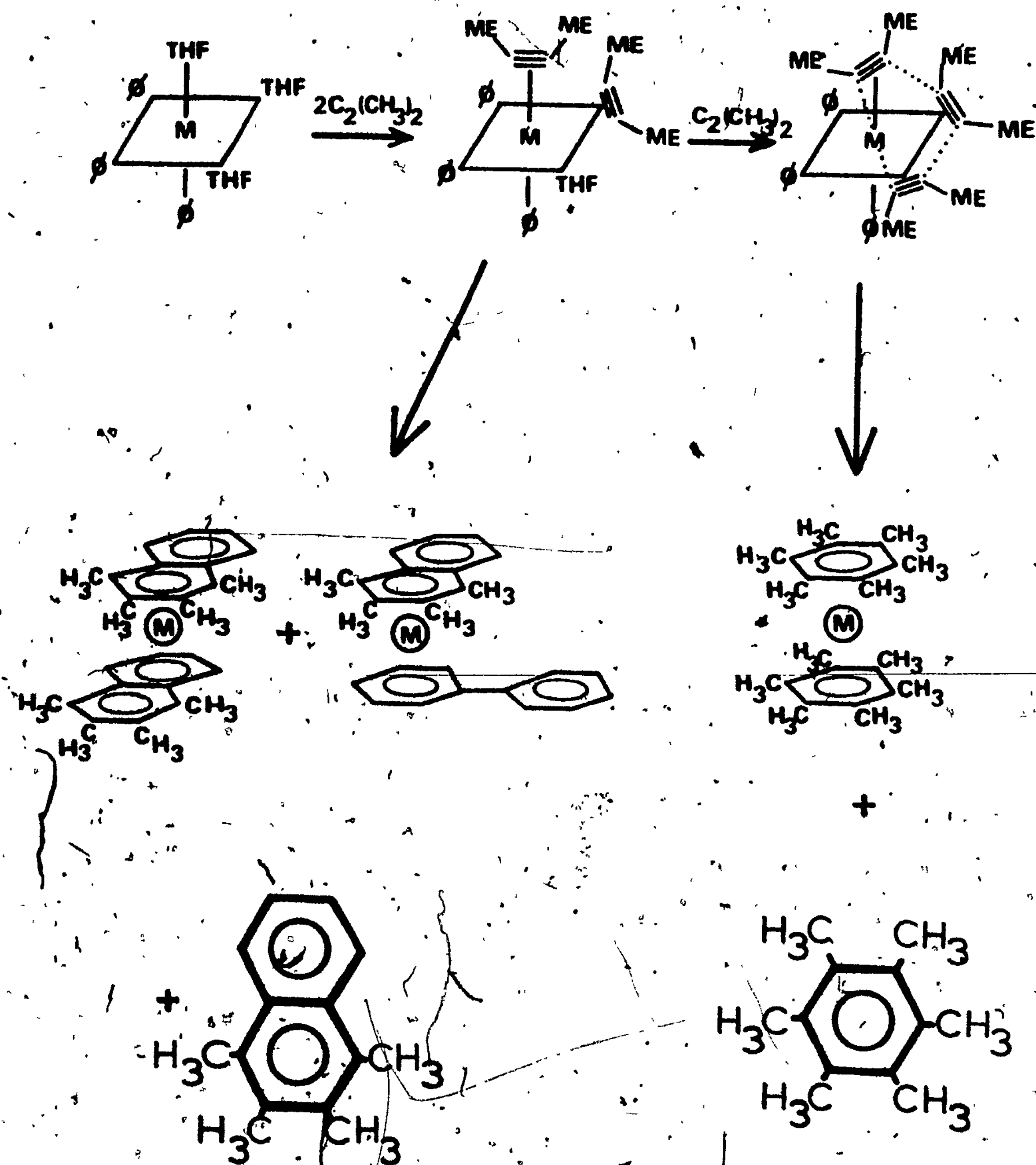
Triphenylchromium(III) tetrahydrofuranate is an octahedral d^2sp^3 system in which the tetrahydrofuran is essential to the stability of triphenylchromium. The tetrahydrofuran ligands can be replaced however and, since they are indiginous to one triangular face of the octahedron, the replacing ligands might well be expected to be in a position to react together. Addition of acetylene or monosubstituted acetylenes to a tetrahydrofuran solution of triphenylchromium(III) causes rapid and uncontrolled polymerization of the acetylene. When the acidic hydrogen is absent, as in the case of disubstituted acetylenes, a controlled reaction is observed.

The products of this reaction are dependent on the ratio of acetylene to triphenylchromium(III) adduct used. The reaction sequence and the proposed intermediates are shown in Figure V-A-10. It will be noted that both the aromatic hydrocarbon desired and an intermediate π-arene complex are isolated. This method can be used in the synthesis of bis-arene complexes.

The synthesis of hexamethylbenzene from 2-butyne can be accomplished by reacting cobaltous chloride and mesitylmagnesium bromide in tetrahydrofuran to give a slurried solution of dimesitylcobalt(II). To this slurry was added the acetylene and the mixture was refluxed. The tetrahydrofuran was replaced by diethylether and the solution was treated with water. The organic layer was dried and hexamethylbenzene was obtained upon evaporation. Treatment of the water layer with tetraphenylboron yielded the dihexamethylbenzenechromium(I) as its tetraphenylborate salt. A similar trimerization reaction sequence involving manganese has also been developed.

Arnett, Strem and Friedel[83] reported the synthesis of di(2,2,5,5-tetramethyl-3,4-hexyne)hexacarbonyl-

Figure V-A-10. Summary of the cyclic trimerization of 2-butyne using triphenylchromium(III).


THF
THF
THF
M
ø
2C2(CH3)2
ME
ME
ME
ME
C2(CH3)2
ME
H3C
CH3
M
+

dicobalt(0) (($^tBu-C{\equiv}C-Bu^t$)$Co_2(CO)_6$) and its reaction with six moles to t-butylacetylene to form 1,2,4,5-tetra-t-butylbenzene. No mechanistic arguments were presented. In the same year, 1,2,4-tri-t-butylbenzene was synthesized[379] by the bromine decomposition of $(HC{\equiv}CBu^t)_3Co_2(CO)_4$. The authors of this work put forth the hypothesis that this complex consisted of a seven-membered metallocyclic ring as shown in Figure V-A-11a.

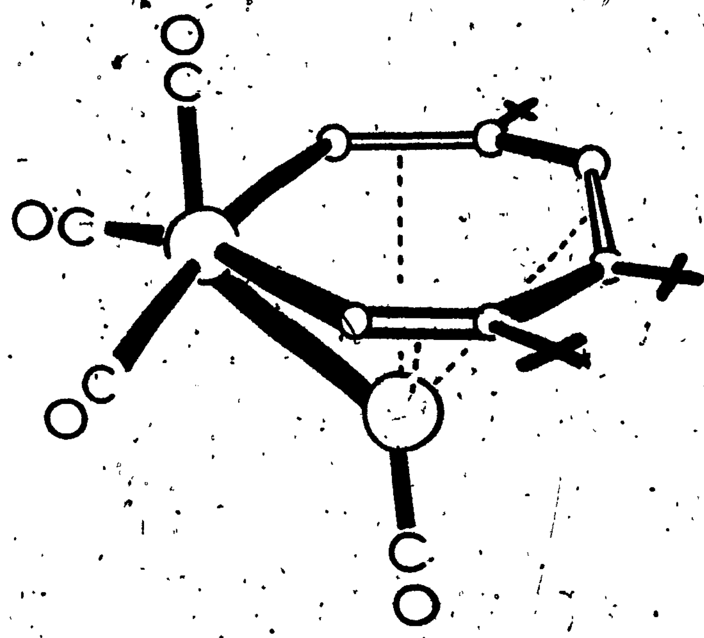
In 1964, Mills and Robinson[380] proved by an X-ray crystallographic structure determination that the complex $(HC{\equiv}CBu^t)_2(HC{\equiv}CH)Co_2(CO)_4$ has a diallyl type of 'flyover bridge' structure as shown in Figure V-A-11b. Another intermediate in the cyclic trimerization of acetylene had been found. It will undoubtedly not be the last.

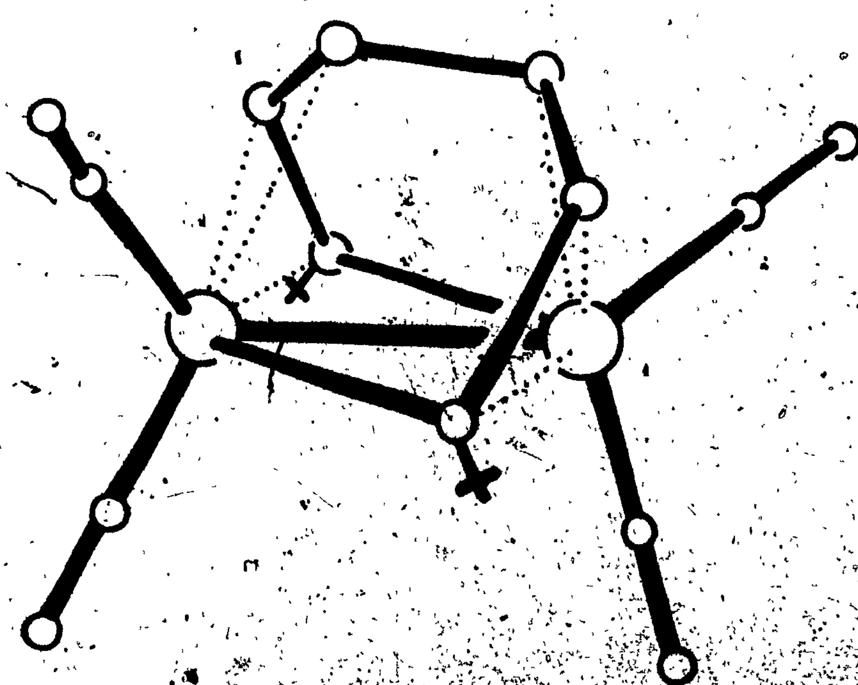
5. <u>Arene Tetracobalt Enneacarbonyls</u>

Steinberg, Wender and Orchin[381] have described an analytical method for the determination of the amount of dicobaltoctacarbonyl remaining in an incomplete reaction sequence. Stirring the carbonyl in benzene solution

Figure V-A-11a. Seven-membered metallocyclic ring intermediate proposed by Kruerke, Hübel and Hoogzand for the complex $(HC\equiv CBu^{t})_3Co_2(CO)_4$.[379]

Figure V-A-11b. The X-ray crystallographically-determined structure of the complex $(HC\equiv CBu^{t})_2(HC\equiv CH)\cdot Co_2(CO)_4$.[380]


OC
OC
C
O
C
O



produced a dark precipitate which was not identified and the liberation of 40% of the available carbon monoxide.

Hieber, in two independent reports,[382,383] published the results of the reaction of dicobaltoctacarbonyl with benzonitrile and aniline. Two benzonitrile complexes recovered are claimed to be $Co(C_7H_5N)_{1.9}(Co(CO)_4)_2$ and and $Co(C_7H_5N)_6(Co(CO)_4)_2$. Aniline also reacts with dicobaltoctacarbonyl to give the complex $Co(C_6H_7N)_2(Co(CO)_4)_2$ which subsequently decomposes to tetracobaltdodecacarbonyl, cobalt metal and aniline.

Fischer and Berkert[384] simultaneously with Chini and Ercoli[385] published the results of the reaction of dicobaltoctacarbonyl with benzene or toluene at 80°C in the presence of aluminum bromide. The results reported here are those of the latter group. It is claimed by these authors that the intermediate in the reaction sequence is $Co_2(CO)_8 \cdot AlBr_3$. This subsequently reacts with the arene to give the cation $Co_3(CO)_2(arene)_3^{-}$ which was isolated as its iodide, bromide and tetraphenylborate salts.

The structure of this ionic species is presumed to be described by a triangle of cobalt atoms, each atom of which is π bonded to an arene. The two carbonyl ligands are assumed to be each bonded to the three cobalt atoms forming a three-centered bridge. No structural studies have been accomplished other than infrared spectral interpretation. Chini and Ercoli claim that, in the absence of the aluminum bromide, dicobaltoctacarbonyl "does not react thermally with aromatic hydrocarbons to form π-arene complexes".[386] This statement was proven false but not until thirteen years had passed.

It is most probably a reflection on the degree of reactivity of dicobaltoctacarbonyl that reactions could have been carried out in refluxing benzene (which is an often-used solvent) without formation of a π benzene cobalt carbonyl complex. It is perhaps also a reflection on chemists who do not separate minor products chromatographically that small yields of this π-benzene cobalt carbonyl complex could have been overlooked for such a long time.

Pauson and co-workers published a note [387] in which they describe the reaction of bicyclo{2,2,1}hepta-2,5-diene with acetylenehexacarbonyldicobalt(0) and phenylacetylenehexacarbonyldicobalt(0). When a non-aromatic solvent was used (dimethoxyethane or isooctane), the major product was *pentahapto*cyclopentadienyldicarbonylcobalt(II). However, when the solvent was benzene or toluene, refluxing the reactants gave the aforementioned product in minor yield. The major product here was (arene)$Co_4(CO)_9$ as determined by chemical analysis, mass spectral and nmr studies. The infrared spectra indicated both bridging and terminal carbonyl stretching bands. The reaction products and the structure proposed for them were those illustrated in Figure V-A-12.

Complexes have been made with xylene, mesitylene and anisole as well. It was found that simple warming of the arene in the presence of tetracobaltdodecacarbonyl or dicobaltoctacarbonyl (which decomposes to tetracobalt-dodecacarbonyl as discussed in the General Introduction of this Thesis) gave the complexes.

A complete infrared study[388] of the toluene-, tetrahydronaphthalene-(tetralin) and mesityleneenneacarbonyl-tetracobalt(0) complexes has recently been published. Table V-A-5 gives the terminal and bridging carbon-oxygen stretching frequencies for these three complexes.

From a study of the observed intensities of the terminal carbonyl stretching modes, the authors place certain constraints on the angle α_1 (formed between the vector joining a basal to an apical cobalt atom and the vector defined by the same basal cobalt and the carbonyl carbon atom) and α_2 (the angle subtended at the basal cobalt defined by the two terminal carbonyl carbons). It is claimed that α_2 should be within the range $90^\circ<\alpha_2<104^\circ$ whereas the upper limit for $\alpha_1 + \alpha_2$ should be 215.3°. It is

Figure V-A-12. A schematic representation of the reaction studied by Pauson *et al.*[387,389]

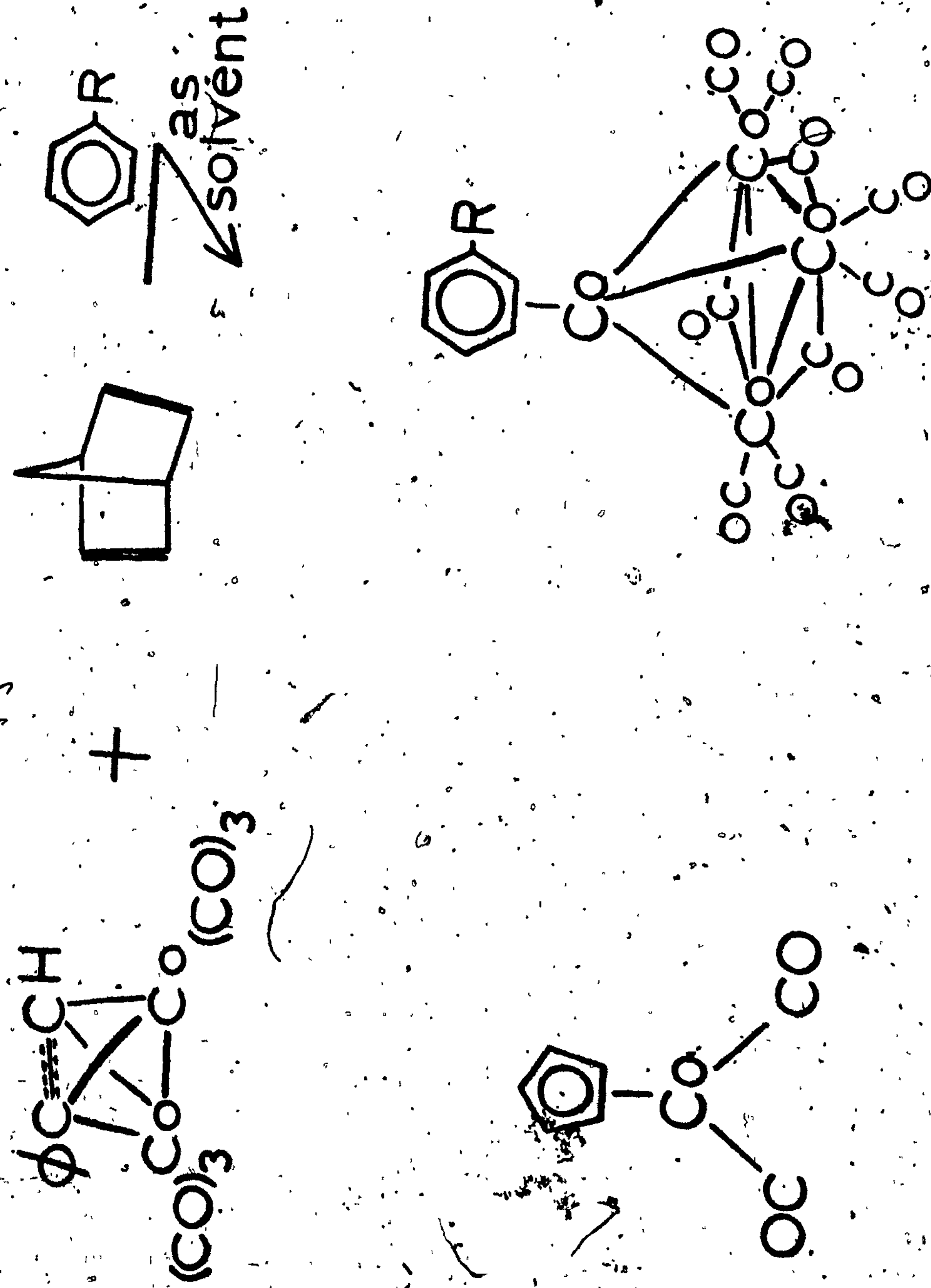

as solvent

TABLE V-A-5

CARBONYL STRETCHING FREQUENCIES (cm^{-1}) OF (ARENE)$Co_4(CO)_9$ COMPOUNDS

ARENE	TERMINAL C-O FREQUENCIES				BRIDGING
Toluene	2074.5 (s)	2031.2 (vs)	2013.0 (s)	1999.8 (m)	1829.0
Tetralin	2073.1 (s)	2029.4 (vs)	2011.8 (s)	1998.6 (m)	1856 1829-1825
Mesitylene	2072.0 (s)	2028.8 (vs)	2009.6 (s)	1996.8 (m)	1829.0

also noted that there is an increase in the angle α_1 due to steric interactions in the arene order toluene < tetralin < mesitylene.

To amplify their note, Pauson *et al.*[389] published a full paper in May, 1973 on the arene enneacarbonyltetracobalt(0) complexes studied by them. Little is said about the infrared spectra of these compounds. Values of 2065(s), 2020(vs), 2003(s) and 1990(m)cm^{-1} are quoted for the terminal and 1820cm^{-1} for the bridging carbonyl bands. All values are to within ± 5 cm^{-1}.

In contrast, the nmr investigation appears to be quite thorough. The aromatic protons absorb about 1.2 ppm to higher field than the parent arenes. The ring protons of benzene absorb at 6.17 δ in a carbon disulphide solution of benzeneenneacarbonyltetracobalt(0). The other arenes absorb around the same region.

The arenes used, the yields (based on the norbornadiene-phenylacetylene-dicobalthexacarbonyl reaction) and nmr data are summarized in Table V-A-6. The methoxybenzenes appeared to give the most unstable complexes reported. Chlorobenzene is claimed to form a very unstable complex but in trace amounts. The authors have been unable to isolate the arene-rhodium analogs.

TABLE V-A-6

(ARENE)$Co_4(CO)_9$ COMPLEXES SYNTHESIZED BY PAUSON *et al.*[389]

ARENE	YIELD (%)	RING PROTONS CHEMICAL SHIFT (δ)
Benzene	36%	6.17
Toluene	28%	6.05
Ethylbenzene	19%	6.00
o-xylene	36%	5.95
m-xylene	37%	5.92 (middle)
p-xylene	39%	5.93
mesitylene	49%	5.90
1,2,4,5-tetramethylbenzene	35%	Not Reported
Pentamethylbenzene	22%	Not Reported
Hexamethylbenzene	21%	----
Anisole	15%	6.07, 5.73
2-methylmethoxybenzene	18%	Not reported
4-methylmethoxybenzene	20%	Not reported
3,5-dimethylmethoxybenzene	23%	Not reported

In this paper the authors state that D.W. Hudson and O.S. Mills have confirmed the structure of the greenish-black *p*-xyleneenneacarbonyltetracobalt(0) complex by X-ray diffraction although no results have as yet been published.

SECTION B. EXPERIMENTAL

1. Synthesis of Xyleneenneacarbonyltetracobalt(0)

2,2,5,5-tetramethyl-3-hexyne ($C_{10}H_{18}$, 0.60 g, 4.4 millimoles) in 25 ml hexane was added to 1.50 g (4.4 millimoles) dicobaltoctacarbonyl ($Co_2(CO)_8$) in 50 ml hexane. The reaction mixture was refluxed (69°C) for 18 hours and then cooled. The solvent was evaporated to 5 ml and this was placed on a chromatographic column. The column was 2 inches in diameter and 18 inches long. The silica gel, used to pack the column wet, was previously deactivated with water (40% w/w).

A black insoluble powder stayed at the top of the column. Two bands were observed to separate well. The first was deep red and was eluted using hexane. The solvent was evaporated completely from the red solution to yield 1.14 g of red crystals which constituted the anticipated product $Co_2(CO)_6(C_{10}H_{18})$ in 61% yield. Decomposition occurred at 220°C in accordance with the original paper on the preparation of the complex.[83] The infrared spectrum and mass spectrometric analysis gave results which positively identified the red solid as di-t-butylacetylenehexacarbonyldicobalt(0).

The second band on the column was olive-green and was slow moving with hexane. It was eluted (using chloroform) as a single band and the solvents were removed *in vacuo*. A weight of 0.12 g of this green complex was obtained which corresponds to 9.2% of the available cobalt based on $Co_4(CO)_9$(xylene).

The solid was investigated by infrared spectroscopy using the NUJOL mull and the carbon disulphide solution techniques. The results of such an investigation are presented in Table V-B-1. The complex was also examined in a cursory manner by mass spectrometric analysis. Two strong peaks dominated the spectrum, the next strongest peak being but 8% the intensity of the first two. These two peaks were at *m/e* 91 and *m/e* 106. Peaks higher than *m/e* 106 were small if at all perceptible.

The sample decomposed without melting in the range 139→142°C. The solid, upon heating, appeared to moisten just before a liquid appeared in the capillary tube. Brown-red crystals formed in the colder section of the capillary as confirmed by microscopic examination.

2. Purification and Use of ANACHEMIA Hexane

500 ml of solvent hexane were treated with 100 ml concentrated sulphuric acid. The two phases were

TABLE V-B-1

INFRARED PEAKS[a] (cm^{-1}) FOR (*o,m*-XYLENE)ENNEACARBONYLTETRACOBALT

2960(m)†	1287(m)†
2924(s)†	1270(m)†
2870(m,sh)†	1262(m,sh)†
2857(m)†	1135(w,sh)†
	1122(w)†
2077(s)	1072(w)†
2032(vs)	1037(w)†
2015(vs)	
1997(m)	838(w)†
1966(w)†	827(w)†
1822(s)	540(m)
1730(m)†	516(m)
	480(w)
1380(w)†	426(m)

[a] Unless otherwise indicated, all frequencies were recorded in the form of their NUJOL mulls on KBr windows using the IR-457 (±3 cm^{-1}). Those peaks marked with a † were recorded by IR-457 (±3 cm^{-1}) of carbon disulphide solution using 1.0 mm sodium chloride matched cells.

stirred vigorously while refluxing for a period of three hours. The mixture was cooled and the sulphuric acid layer was removed. Two hundred milliliters of water (containing sodium bicarbonate) were added to the hexane layer and the salting-out procedure gave hexane free from aromatics. Excess water was removed and the hexane was refluxed over calcium hydride for one week.

The synthesis described in Part 1 of this Section was repeated and work-up using column chromatography gave no indication of the olive-green complex. Only tetracobaltdodecacarbonyl was recovered. Dicobaltoctacarbonyl was dissolved in <u>untreated</u> ANACHEMIA hexane and refluxed for 24 hours. A small olive-green band was observed with column chromatography. The same experiment was repeated using the <u>treated</u> ANACHEMIA hexane but no green band was observed.

3. Synthesis of Benzeneenneacarbonyltetracobalt(0)

1.50 g of dicobaltoctacarbonyl (4.4 millimoles) was dissolved in 75 ml reagent grade benzene. With constant stirring under a nitrogen atmosphere, the solution was refluxed for 21 hours. The solution turned dark brown during the first ten hours of reaction. Then a metallic mirror formed on the inner surface of the flask and an insoluble black powder was observed to form. The solution slowly turned from brown to olive-green.

The solution was cooled and filtered to remove the small amount of black paramagnetic powder which had formed. The benzene was then removed *in vacuo* at room temperature and the remaining black solid was redissolved in hexane to give an olive-green solution. The filtered hexane solution, stoppered under nitrogen, deposited crystals of benzeneenneacarbonyltetracobalt at $0^{o}C$ and these were removed from the solution, washed with cold hexane and dried *in vacuo*. 0.65 g of benzeneenneacarbonyltetracobalt was obtained which represents a 52% yield based on dicobaltoctacarbonyl.

The solid complex was obtained in the form of fine needles which were unsuitable for X-ray crystallographic analysis. These crystals decomposed without melting to give a liquid (benzene presumably) and a cobalt mirror in the range $145\rightarrow147^{o}C$. In other synthetic procedures similar to that described above, a grey powder was obtained which redissolved completely to give a green solution. Examination under the microscope indicated a surface deterioration (probably due to oxidation) was responsible for the grey colour. The large decomposition range of $152\rightarrow158^{o}C$ supported the argument that this form of the complex was impure. Finally, rhombohedral-like crystals (without surface deterioration) were obtained when extra care was exercised to exclude oxygen. These crystals, which were opaque to transmitted light and appeared black to reflected light, decomposed without melting in the range 139-141°C. They were used for crystal structure determination and all other chemical and physical investigations. Chemical analysis gave %C - 31.91, %H - 1.22 and %Co - 41.32. The theoretical analysis for $C_{15}H_6Co_4O_9$ is %C - 31.84, %H - 1.07 and %Co - 41.65.

The infrared spectrum of benzeneenneacarbonyltetracobalt(0) was recorded in its NUJOL mull form. The results of these investigations are presented in Table V-B-2.

4. The Synthesis of Tetracobaltdodecacarbonyl

Tetracobaltdodecacarbonyl ($Co_4(CO)_{12}$) was prepared[26] by refluxing dicobaltoctacarbonyl in ligroin at 66°C for a day or two. The solvents were removed and the solutes redissolved in hexane. The solution was chromatographed on a silica gel/hexane column which had been deactivated with 15% (w/w) water. The $Co_4(CO)_{12}$ band was eluted with hexane, the solvent was evaporated to concentrate the solution and this was kept at 0°C under nitrogen gas overnight to precipitate large black crystals of $Co_4(CO)_{12}$ which were washed with cold hexane, dried *in vacuo* and

TABLE V-B-2

INFRARED PEAKS[a] (cm^{-1}) FOR BENZENEENNEACARBONYLTETRACOBALT

2078 (s)	1030 (w, bd)	
2045 (m, sh)		
2035 (vs)	898 (w)	
2018 (vs)	822 (w, sh)	
1996 (s)	808 (m)	
1965 (w) †	792 (w, sh)	785 (m) †
1824 (s)	546 (m)	
	522 (m)	
1264 (w)	490 (w)	
1095 (w, bd)	436 (m)	

[a] Unless otherwise indicated, all frequencies were recorded in the form of their NUJOL mulls on KBr windows using the IR-457 (±3 cm^{-1}). Those peaks marked with a † were recorded by IR-457 (±3 cm^{-1}) using a carbon disulphide solution of the complex in 1.0 mm sodium chloride matched cells.

stored under nitrogen until used. Care was exercised to ensure that $Co_4(CO)_{12}$ was not obtained in microcrystalline form since, as such, it has a tendency to pyrolize.

5. Synthesis and Characterization of some π-Areneennea-carbonyltetracobalt(0) Complexes

572.0 mg (1.0 millimoles) of the $Co_4(CO)_{12}$ described above (purified by column chromatography) was weighed and dissolved in ligroin. To this was added 1.0 millimoles of one of seven arenes (hexafluorobenzene, hexachlorobenzene, benzene, *o*-xylene, *m*-xylene, 1,3,5-trimethylbenzene and hexamethylbenzene) either as a liquid (from a 1.0 ml syringe) or as a solid. The reaction mixture, under nitrogen gas, was refluxed (66.2°C) in each case for exactly 26 hours, at which point reaction was assumed to be complete.

The reaction mixture was allowed to cool and the solvent was evaporated to dryness. Hexane was used to redissolve the solutes and this solution was eluted through a chromatographic column 1½ inches wide and 12 inches long packed with untreated silica gel in hexane. The first band, when present, was $Co_4(CO)_{12}$ and this was eluted with hexane. The solvents were removed *in vacuo* and the $Co_4(CO)_{12}$ was dried and weighed.

The second olive-green band remained on the column and was removed with dichloromethane (CH_2Cl_2) after the $Co_4(CO)_{12}$ had been removed. In most cases the solution was stable to air oxidation for short periods of time and thus could be handled conveniently. The solvents were removed *in vacuo* and the green-black solid so obtained was dried for a 12 hour period. The weight of this product was obtained.

This experimental sequence was repeated using dicobaltoctacarbonyl (684.0 mg , 2.0 millimoles) instead of $Co_4(CO)_{12}$. The reaction was allowed to proceed for 36 hours in this case rather than 96. The quantities of reactants used and percentage yields for the various π-areneenneacarbonyltetracobalt(0) complexes formed by the two methods are given in Tables V-B-3 and V-B-4 for the $Co_4(CO)_{12}$ and $Co_2(CO)_8$ starting materials respectively. Table V-B-3 also quotes the approximate decomposition temperature ranges for the π-arene complexes formed. All complexes decomposed giving the free arene (liquid droplets or solid crystals condensed on the upper portion of the capillary tube), sublimed crystals of $Co_4(CO)_{12}$ (identified by infrared spectroscopy) and a black powder residue surrounded by a cobalt mirror.

The benzeneenneacarbonyltetracobalt(0) complex was subjected to chemical analysis as indicated earlier.

TABLE V-B-3

$Co_4(CO)_{12}$ + Arene $\rightarrow$ (Arene)$Co_4(CO)_9$ + 3CO$\uparrow$

Arene	Quantity of Arene Reacted with 1 millimole (572 mg) $Co_4(CO)_{12}$		Yield of product g %	$Co_4(CO)_{12}$ recovered g %	Decomposition Temperature Range °C
C_6F_6	186 mg	0.12 ml	0.0209 g 3.1%	0.4673 g 81.7%	143→145
C_6Cl_6	285 mg		0.2417 g 31.4%	0.2631 g 46.0%	142→144
C_6H_6	78 mg	0.09 ml	0.2193 g 38.6%	0.1204 g 21.0%	139→142
o-xylene	106 mg	0.12 ml	0.2592 g 43.6%	0.0150 g 2.6%	139→143
m-xylene	106 mg	0.12 ml	0.2654 g 44.7%	0.0702 g 12.3%	138→140
$C_6H_3(CH_3)_3$	120 mg	0.14 ml	0.4796 g 78.9%	---	158→160
$C_6(CH_3)_6$	162 mg		0.5798 g 89.2%	---	162→165

TABLE V-B-4

$$2Co_2(CO)_8 + \text{Arene} \rightarrow (\text{Arene})Co_4(CO)_9 + 7CO\uparrow$$

$$2Co_2(CO)_8 \rightarrow Co_4(CO)_{12} + 4CO\uparrow$$

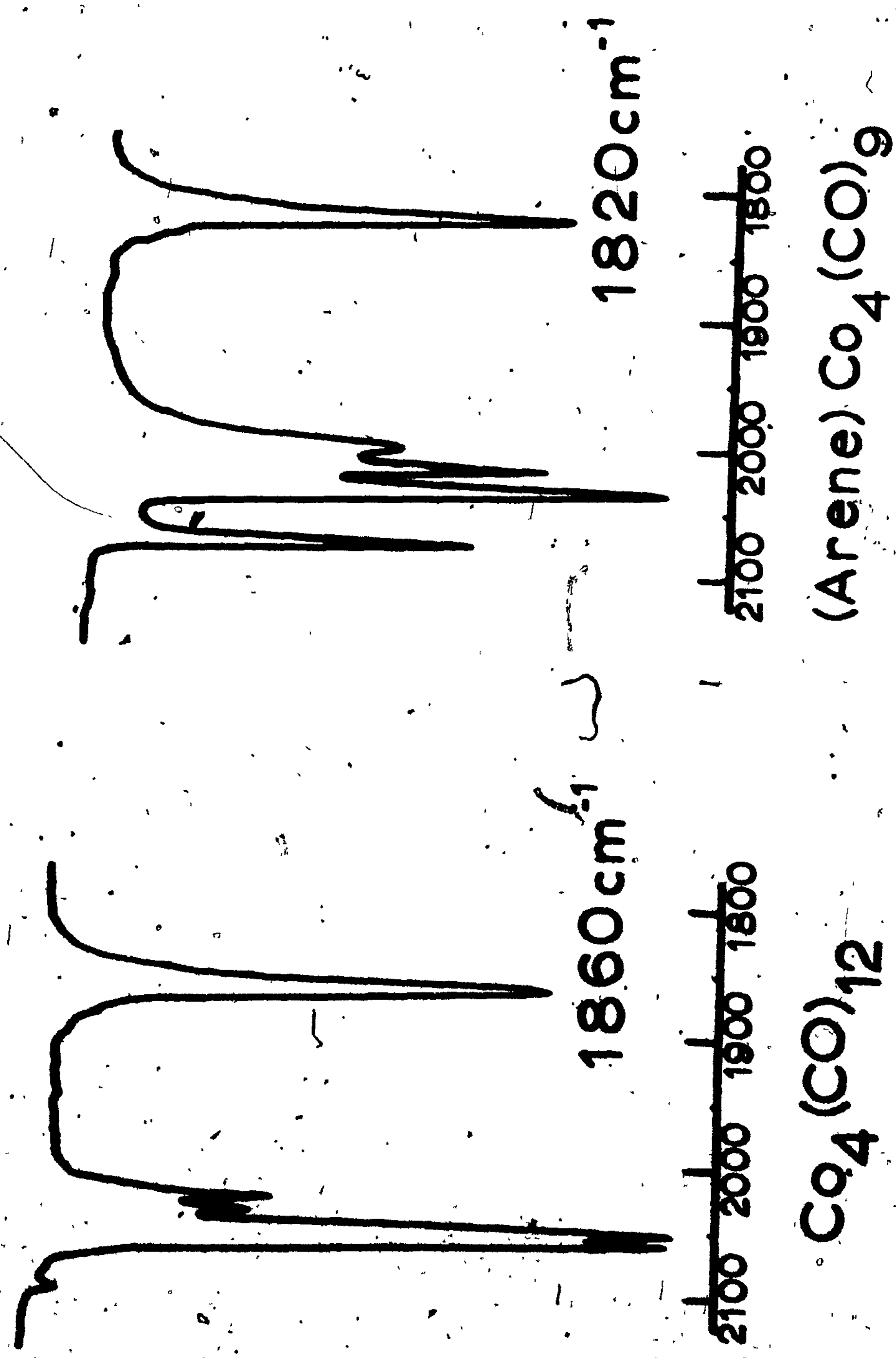
Arene	Quantity of Arene Reacted with 2 millimoles(684 mg) $Co_2(CO)_8$		Yield of product g %	$Co_4(CO)_{12}$ recovered g %	Infrared Frequencies in Stretching Carbonyl Region (cm^{-1})					
					s	vs	vs	s	w	s
C_6F_6	186 mg	0.12 ml	0.0153 g 2.5%	0.5841 g 85.4%	2077	2031	2012	1997	1963	1814
C_6Cl_6	285 mg		0.2228 g 28.9%	0.4628 g 60.3%	2075	2029	2010	1994	1962	1817
C_6H_6	78 mg	0.09 ml	0.1200 g 38.8%	0.1522 g 26.6%	2078	2033	2015	1997	1964	1823
o-xylene	106 mg	0.12 ml	0.2471 g 41.6%	0.1074 g 15.7%	2077	2032	2012	1997	1963	1820
m-xylene	106 mg	0.12 ml	0.2560 g 43.1%	0.1973 g 34.9%	2078	2038	2018	1997	1962	1820
$C_6H_3(CH_3)_3$	120 mg	0.14 ml	0.4453 g 76.3%	0.0185 g 2.7%	2076	2033	2014	1994	1961	1816
$C_6(CH_3)_6$	162 mg		0.5461 g 84.6%	---	2077	2032	2015	1992	1961	1808

It was decided not to send all (arene)$Co_4(CO)_9$ complexes for analysis since their infrared spectra in the carbonyl stretching region were sufficiently characteristic to afford proper identification. However, the hexamethylbenzene-enneacarbonyltetracobalt(0) complex was verified by analysis and the results agreed. The experimental %C = 38.94, %H = 2.80 and % Co = 35.94 whereas the theoretical values based on $C_{21}H_{18}Co_4O_9$ are %C = 38.80, %H = 2.79 and %Co = 36.26.

Infrared spectra were recorded in carbon disulphide solution for all seven complexes. The positional and intensity patterns of carbonyl stretching frequencies are characteristic of these complexes and can be readily distinguished from those of the $Co_4(CO)_{12}$ precursor. The infrared spectra for both the $Co_4(CO)_{12}$ and the product complexes are shown, for the 1800 to 2100 cm^{-1} region, in Figure V-B-1. Absorptions for the various complexes are listed in Table V-B-4.

Attempts were made to synthesize other (arene)$Co_4(CO)_9$ complexes. The experimental procedures were the same as those described for the seven arene complexes discussed above. For aniline, trihydroxybenzene and tri-nitrobenzene, no product was observed. Trace amounts of green product were observed for the toluene and ααα-tri-fluorotoluene reactions. The *p*-xylene complex was formed

Figure V-B-1. Infrared spectra (1800→2100 cm^{-1}) of tetracobaltdodecacarbonyl and (arene)enneacarbonyltetracobalt(0) in carbon disulphide solution.


1820cm-1
2100 2000 1900 1800
(Arene) Co4(CO)9
1860cm-1
2100 2000 1900 1800
Co4(CO)12

in 37% yield with $Co_4(CO)_{12}$ and the hexaethylbenzene-enneacarbonyltetracobalt(0) compound was formed in even higher yield. Physical data on these compounds were not recorded. Dicobaltoctacarbonyl was dissolved in benzonitrile and the solution was heated to 130°C and stirred for 68 hours at this temperature. Two products were obtained. The first was isolated upon heating the solution to remove the excess benzonitrile. It was a green solid insoluble in most common solvents. The second product, a red insoluble solid, was obtained upon cooling the benzonitrile solution. It was assumed both products were polymeric.

6. The Crystal and Molecular Structure of the Disordered Xyleneenneacarbonyltetracobalt(0) Complex

Recrystallization of the olive-green solid from hexane gave rhombohedral-like crystals. A crystal approximately 0.2 x 0.2 x 0.2 mm was mounted on a eucentric head and Weissenberg photography was initiated. The oscillation photographs displayed the absence of any symmetry. The zero level Weissenberg showed what appeared to be two identical axes separated by approximately 94°. These were labelled a^* and b^*, the rotation axis arbitrarily assigned as c. There was no 'right-left' symmetry about the axes.

Zero level precession zones were obtained for both the a^*c^* zone and the b^*c^* zone. The intensity pattern and spacing for all three reciprocal axes were identical from a scrutiny of these zero level photographs. No extra symmetry conditions were implied by the first level precession zones so the space group was assigned as R3 (No. 146) or R$\bar{3}$ (No. 148). The precession photographs were measured and $y_a = y_b = y_c = 4.25$ mm. The angle was measured as 94°. By application of Equation II-B-1, the reciprocal axis length was computed as 0.099^{573} Å^{-1}. Reducing the triclinic relationships to Equations V-B-1 and V-B-2, the direct cell axis length was computed to be 10.096Å and the direct cell angle was 85.7°.

$$a = \frac{\text{sine } \alpha^*}{a^* \sqrt{1 - 3\cos^2\alpha^* + 2\cos^3\alpha^*}} \qquad \text{V-B-1}$$

$$\cos\alpha = \frac{\cos^2\alpha^* - \cos\alpha^*}{\text{sine}^2\alpha^*} \qquad \text{V-B-2}$$

The goniometer head was mounted on the diffractometer and the (2,0,0) and the (0,2,0) reflections were located and centered. These two reflections plus the approximate unit cell constants determined from the photographs were used to calculate an orientation matrix that successfully predicted the position of the third reciprocal axis reflection (0,0,2). Since the intensities of all diffraction spots on all three axes were identical, care was exercised to ensure that the correct axes were chosen. Relative intensities of planes not on the axes were compared to ensure the correct identification of the reflections centered and used in the least squares refinement of the cell constants in the rhombohedral setting. These were the (5,0,0), (-5,0,0), (0,5,0), (0,-5,0), (0,0,5), (0,0,-5), (4,-3,0), (-4,3,0), (3,0,-4), (-3,0,4), (1,4,-2) and (-1,-4,2) reflections. The cell constants for the rhombohedral cell after two cycles of refinement were $a = 10.046 \pm 0.005$Å and $c = 85.45 \pm 0.02^{\circ}$. The unit cell volume is thus 1004.Å^3. The observed density of 1.87g cm^{-3}, measured by flotation in zinc iodide aqueous solution, indicated two molecules per unit cell. The space group R$\overline{3}$ was chosen to describe the correct cell symmetry and the molecular volume was predicted to be 502.Å^3. The calculated density ($Z = 2$, $F.W. = 593.6$, $V = 1004.$ Å^3) was 1.96g cm^{-3}.

It was deemed convenient to use a hexagonal setting for data collection. The conversion from rhombohedral (rhom) indexing to hexagonal (hex) indexing [391] is given by V-B-3. The indices of the three rhombohedral axes reflections used to define the cell were converted and used with their refined 2θ, ω, χ and ϕ angles to give a new orientation matrix with the hexagonal cell constants. A least squares refinement of the hexagonally-indexed reflections gave $a_{hex} = b_{hex} = 13.633 \pm 0.007$ and $c_{hex} = 18.73 \pm 0.01$Å.

$$\begin{aligned} h_{hex} &= h_{rhom} - k_{rhom} \\ k_{hex} &= k_{rhom} - l_{rhom} \qquad \text{V-B-3} \\ l_{hex} &= h_{rhom} + k_{rhom} + l_{rhom} \end{aligned}$$

Data collection was started in the hexagonal setting. It became apparent that changes were occurring in the crystal when symmetry-related reflections were found to differ significantly in intensity when checked. The reason for the verification was a broadening of the diffraction peaks and the rather large decrease in the intensity of the three check reflections. A scan of the three rhombohedral axes at this point showed that the c^*_{rhom} axis reflections were consistently lower that those on the other two axes (Table V-B-5). At this point, it was thought advisable to re-examine the crystal by Weissenberg photography. The rhombohedral a^*b^* zone was still present but the diffraction spots were very diffuse. The c^* axis, from the diffractometer scan, certainly was no longer the same.

The original sample of crystals was searched for another rhombohedral crystal but to no avail. All crystals examined were monoclinic, even those obtained from subsequent recrystallisations. It was decided to discontinue the investigation of the rhombohedral form and use the persistent monoclinic crystals.

TABLE V-B-5

THE COUNTING PARAMETERS FOR SOME RHOMBOHEDRALLY-RELATED AXES REFLECTIONS IN THE XYLENEENNEACARBONYLTETRACOBALT(0) STRUCTURE

Rhombohedral Indices	Background Low	Background High	Scanning Time (sec)	Uncorrected Count	Corrected Count
2 0 0	77	137	152.80	1658	840
0 2 0	93	187	152.58	1928	860
0 0 2	48	75	152.76	713	243
3 0 0	127	69	154.61	1018	261
0 3 0	142	86	154.61	1148	267
0 0 3	61	34	154.61	435	68
4 0 0	46	43	155.77	414	67
0 4 0	63	58	155.65	551	80
0 0 4	28	22	155.57	232	38
5 0 0	40	39	157.47	519	208
0 5 0	56	54	157.45	639	206
0 0 5	25	22	157.69	242	56
6 0 0	31	29	158.54	278	40
0 6 0	41	36	158.76	355	49
0 0 6	19	16	158.57	145	6
7 0 0	25	26	160.56	213	8
0 7 0	38	31	160.55	286	9
0 0 7	16	15	160.43	123	0

A brick-shaped crystal, approximately 0.1 x 0.2 x 0.1 mm in size, was mounted on a eucentric goniometer head along its longest dimension. Oscillation photographs showed *mm* symmetry and a zero level Weissenberg gave a representation of the monoclinic a^*c^* zone. An upper level Weissenberg revealed the *c* glide plane perpendicular to *b*. Precession zones a^*b^* and b^*c^* confirmed the space group as $P2_1/c$ (No. 14) with the use of arguments identical to those provided in Section III-B of this Thesis. It was noted that the β^* angle (85.4° by azimuthal angle setting difference) was similar to the rhombohedral cell angle. A striking similarity also existed between the $h0l$ monoclinic zone and the $hk0$, $h0l$ and $0kl$ zones of the rhombohedral.

The values of y_a, y_b and y_c from precession zone measurements were 4.29, 4.32 and 2.11 mm respectively. The β^* angle was 85.4°. Conversions to reciprocal cell dimensions by Equation II-B-1 and application of reciprocal-to-real-cell relationships[124] gave the following approximate cell constants: $a = 9.97$, $b = 9.87$, $c = 20.27$ Å, $\beta = 94.5^{\circ}$. The density was measured by flotation in aqueous zinc iodide solution. A value of $1.87(2)$ g cm^{-3} was obtained which indicated that there were four molecules in the unit cell ($Z = 4$, $F.W. = 593.6$, $V = 1990.6$ Å^3; $\rho_{calc} = 1.98$ g cm^{-3}).

The goniometer head was mounted on the diffractometer and the (2,0,0) and the (0,0,3) reflections were located and centered. With the raw cell parameters, a rough orientation matrix was calculated and the (0,2,0) reflection was found and centered. The twelve reflections centered at plus and minus 2θ were the (5,0,0), (-5,0,0), (0,4,0), (0,-4,0), (0,0,10), (0,0,-10), (0,6,9), (0,-3,-8), (0,3,-8), (0,-3,8), (4,0,6) and (-4,0,-6). Two cycles of least squares refinement gave the following accurate cell parameters: $a = 10.03 \pm 0.01$, $b = 9.86 \pm 0.01$, $c = 20.24 \pm 0.02$Å, $\beta = 96.40(5)^\circ$. The unit cell volume was calculated to be 1990.6 Å^3 and this gives a molecular volume of 497.7 Å^3.

Data collection was initiated using the parameters listed in Table V-B-6. The quarter sphere collected was that bounded by positive h and positive k. The l index was allowed to vary from -21 to +21. There were exactly 3000 reflections collected. Of these, 1822 were accepted, 819 were less than 3σ and 359 were considered absent. A reject routine eliminating systematically-absent reflections along with reflections of negative l on the $0kl$ zone was used. Absorption corrections were not applied ($\mu = 34.29$ cm^{-1}).

The structure was solved using the direct method. *NORMA* was used to compute normalized structure factors E_{hkl}. The value of ε was set to 1 for all reflections except those on the $0kl$ zone and on the $0k0$ axis where it was 2. There were 1822 reflections processed, 669

TABLE V-B-6

DATA COLLECTION PARAMETERS FOR XYLENEENNEACARBONYLTETRACOBALT(0)

Radiation used:		Mo K_α (λ = 0.71069Å)	
Pulse height analyzer		100%	
Upper level		6.50	
Lower level		2.50	
Attenuators		Not Used	
Space group routine used:		$P2_1/c$	
maximum h:	10	minimum h:	0
maximum k:	10	minimum k:	0
maximum l:	21	minimum l:	-21
maximum 2θ:	45.0°	minimum 2θ:	4.0°
Standards used (hkl)		(0,1,2)	(5,0,0)
Value and variation		66500 ± 12%	2300 ± 13%
Interval		every 30 reflections	
Background		40 second counts	
Base length of scan		2.5°	
Total number of reflections collected:		3000	

having E_{hkl} greater than 1.0, 44 having E_{hkl} greater than 2.0 and 3 with E_{hkl} greater than 3.0.

Two hundred reflections (with an E_{hkl} value greater than 1.50) were used by *REL*. The triples were signed in the order of their decreasing E_{hkl} magnitudes. The signs were treated according to the *NBACK* = 1 option first and according to the *NBACK* = 0 option for the second pass. The same treatment of the origin-determining reflection parities was used as for tris(hexacarbonyl-dicobalt-π-ethynyl)arsine (Chapter III, Section B, Part 3). The value of *PROBK* was 0.08 and *PROB1* and *PROB2* were set to 0.90 and 0.70 respectively. The starting set included the seven reflections listed in Table V-B-7 with their E_{hkl} phased according to the correct solution.

Four of the sixteen phased starting sets gave the same solution in three cycles. The consistency index was 0.99 for all correct solutions, the next highest being 0.80. There were 92 pluses and 108 minuses for the 200 reflections in the correct solution. One of the starting sets predicted the change of two reflection signs in order to arrive at the correct solution. The other two predicted the change of one sign only.

An E-map was computed using the 200 phased reflections from *REL*. Electron density in one-half

TABLE V-B-7

THE STARTING SET FOR THE SUCCESSFUL *REL* SOLUTION OF

XYLENEENNEACARBONYLTETRACOBALT(0)

h	k	l	E_{hkl}
2	4	1	3.15
0	1	2	3.08
1	1	0	2.93
0	1	-2	-3.04
5	2	6	-2.66
0	8	9	2.66
2	5	3	2.64

the unit cell was computed (0 to 1 in x, 0 to 1 in y and 0 to $\frac{1}{2}$ in z) to one-third angstrom resolution. From this map, four cobalt atom positions were found and a structure factor list was calculated. The scale factor used was 0.97. For 1822 reflections, the discrepancy index was 44%.

An observed Fourier based on this structure factor calculation gave the positions of all atoms except the methyl groups on the benzenoid ring system. A structure factor calculation based on the positions of these atoms for 1822 reflections gave a residual index of 34.8%. Isotropic least squares refinement was initiated with temperature factors of 3.0 for cobalt atoms, 3.5 for carbons and 4.5 for oxygens. The results of the least squares cycles are summarized in Table V-B-8. The total number of parameters for isotropic refinement of all atoms except the methyl carbons was 113 and these were all in a single matrix.

After the third isotropic cycle, a difference Fourier was calculated ($Rmax$ = 3.20). Three peaks were observed near adjacent benzenoid carbon atoms. One of the peaks had a normalized electron density of 999 whereas the other two had map maxima of 520 and 410. Although this was not indicated, occupancy factors of 0.5 were introduced for all three peaks. A cycle of refinement (ISO 4) of only the cobalt atoms and the three new peaks (positions, thermal

TABLE V-B-8

STRUCTURE FACTOR INFORMATION FOR XYLENEENNEACARBONYLTETRACOBALT(0)[a]

	BEFORE REFINE-MENT	ISO(1)	ISO(2)	ISO(4)	ANISO (1)	ANISO (2)	ANISO (3)	ANISO (4)
Scale Factor	0.7543	0.7589	0.7614	0.7731	0.7764	0.7754	0.7779	0.7779
Number of Matrices		1	1	1	2	1	2	2
Total # of parameters		113	113	32[b]	268	64[b]	265	
Number of reflections	1883	1883	1883	1883	1883	1883	1843[c]	
"Goodness of fit"	12.546	4.857	2.997	2.315	1.555	1.397	1.397	1.397
R	34.8	17.6	11.0	9.1	5.9	5.6	5.6	5.6
R (with rejects out)	34.8	17.6	11.0	9.1	5.9	5.6	5.3	5.3
R_w	35.2	18.5	11.4	9.0	5.7	5.4	5.4	5.4
R_w (with rejects out)	35.2	18.5	11.4	9.0	5.7	5.4	5.2	5.2

a The structure factor calculation data listed is for that run immediately AFTER the least squares refinement cycle heading the column. The 3rd ISO cycle is omitted.

b Only the four cobalt atoms and the substituent carbons were refined.

c A reject routine was introduced at this point. Rejected if $(|F_{obs} - F_{cal}|)/F_{obs}$ was greater than 0.50.

parameter and occupancy factor) was undertaken. The other atoms were included in the input but not refined. The occupancy factor for the first peak refined to 0.98, the other two being 0.53 and 0.58. At this point, evidence seemed to indicate the probability that the arene was a mixture of *ortho-* and *meta*-xylene in equal proportions. One of the three substituent crystallographic sites (labelled atom C7) was common to both isomers. For the several cycles the occupancy factors were allowed to vary, they remained in the ratio 1:0.5:0.5 within 5 to 10%. The half-occupancy atoms C8 and C9 were refined isotropically only whereas anisotropic refinement was effected for C7. After ANISO 2 the occupancy factors were set at 1.0, 0.5 and 0.5 respectively and they were no longer refined.

Anomalous dispersion corrections were not applied to this solution. Since more than one matrix was used for anisotropic refinement, the parameters were moved from one matrix to another to ensure some correlation. Anisotropic convergence gave a discrepancy factor of 5.6% and a weighted discrepancy factor of 5.4%. A final difference Fourier (*Rmax* = 3.20) was calculated and the highest peak was 0.6 e$Å^{-3}$. The positions of the three hydrogen atoms on the three non-substituted carbon atoms of the ring were calculated and used in structure factor calculations. They were not found on the difference Fourier map nor were they ever refined.

In almost all cases, the shifts in the 265 refined parameters were two to three times smaller than their estimated standard deviations. A list of observed and calculated structure factors can be found in Appendix D (page 394) of this Thesis. Some weak reflections ($F = 3\sigma(F)$) for which ($|F_{obs} - F_{cal}|/F_{obs}$) was greater than 0.5 are not listed because they were not used in least squares refinement. The final refined positional and thermal parameters for the mixed complex can be found in Appendix D.

7. The Crystal and Molecular Structure of Benzeneenneacarbonyltetracobalt(0)

A sample of the fine fluffy needles of benzeneenneacarbonyltetracobalt(0) was dissolved in hexane and recrystallized to give rhombohedral-like crystals. A parallelopiped with approximate dimensions 0.1 x 0.1 x 0.1 mm was mounted on a eucentric head. No symmetry was observed on the oscillation photograph. The zero level Weissenberg showed two distinct axes about which there was no symmetry. The intensity patterns on the two axes (labelled a^* and b^*) were apparently identical. The a^*c^* precession zone indicated the third axis c^* was the same as the other two.

The reciprocal cell spacings were identical for the three dimensions and the space group was assigned as R3 (No. 146) or R$\bar{3}$ (No. 148). The axis spacing was measured to be 4.43 mm and the α^* angle was 96.2°. The reciprocal cell dimension a^* was calculated (using Equation II-B-1) to be 0.103$_{88}$ Å^{-1}. Thus a and α were found (by Equations V-B-1 and V-B-2) to be 9.76Å and 83°, respectively.

The goniometer head was transferred to the diffractometer and the (5,0,0) and (0,5,0) reflections were found and centered. Assuring a right-handed set of axes, the (0,0,5) reflection was located and centered. An orientation matrix was determined for the diffraction planes. Twelve reflections were centered at plus and minus 2θ and the results were averaged for each reflection. They were the (0,6,5), (0,-6,-5), (0,-6,5), (0,6,-5), (5,0,6), (-5,0,-6), (6,5,0), (-6,-5,0), (5,0,0), (0,5,0), (0,0,5) and (0,0,-5) reflections. After two cycles of refinement, a was found to be 9.798 ± 0.003Å and α = 82.95 ± 0.01°. The unit cell volume was thus 920.$_8$ Å^3. The observed density measured by flotation in zinc iodide aqueous solution, was 1.98$_8$ g cm^{-3}. This implied two molecules in the unit cell and thus space group R$\bar{3}$ (No. 148). The calculated density (Z = 2, $F.W.$ = 565.8 amu, V = 920.$_8$ Å^3) is 2.040 g cm^{-3}. The molecular volume is 460.$_4$Å^3.

It was convenient to collect the data using the hexagonal setting of the rhombohedral cell. The conversion from rhombohedral to hexagonal indexing is given in Equation V-B-3. The conversion of the rhombohedral (5,0,0), (0,5,0) and (0,0,5) indices to the hexagonal (5,0,5), (-5,5,5) and (0,-5,5) indices permitted the calculation (by the Picker Nuclear computer programs) of a hexagonal orientation matrix. The hexagonal unit cell was $a_{hex} = b_{hex} = 12.97$, $c_{hex} = 18.94$Å. Because of the small size of the crystal and a desire for increased accura[illegible] the data were collected in a full hemisphere (positiv[illegible] Only reflections for which $-h + k + l = 3n$ were co[illegible]cted.[392] The data collection parameters are given in Table V-B-9. There were 2693 reflections collected of which 1964 were accepted, 573 were less than 3σ and 156 were considered absent. Absorption corrections were not applied ($\mu = 37.03\ cm^{-1}$).

The indices were transformed back from hexagonal to rhombohedral before the structure was solved or refined. The transformations were as described in Equation V-B-4 where hex abbreviates hexagonal and rhom abbreviates rhombohedral.

$$
\begin{aligned}
h_{rhom} &= (2h_{hex} + k_{hex} + l_{hex})/3 \\
k_{rhom} &= (-h_{hex} + k_{hex} + l_{hex})/3 \qquad \text{V-B-4} \\
l_{rhom} &= (-h_{hex} - 2k_{hex} + l_{hex})/3
\end{aligned}
$$

TABLE V-B-9

DATA COLLECTION PARAMETERS FOR

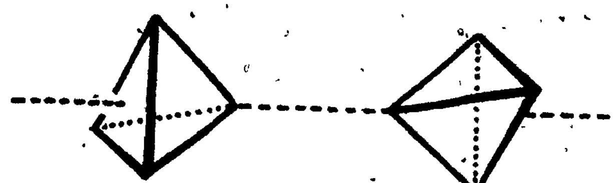
BENZENEENNEACARBONYLTETRACOBALT(0)

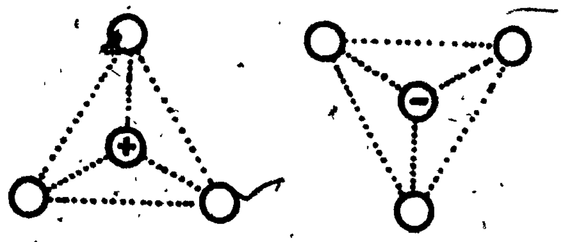
Radiation used:	Mo K_α (λ = 0.71069 Å)
Pulse height analyzer	100 %
Upper level	6.50
Lower level	2.50
Attenuators	Used
Space group routine used:	$R\bar{3}$ (hexagonal axes)
maximum *h*: 13	minimum *h*: 0
maximum *k*: 12	minimum *k*: -13
maximum *l*: 20	minimum *l*: -20
maximum 2θ: 45.0°	minimum 2θ: 4.0°
Standard used (*hkl*)	(0,1,2)
Value and variation	15500 ± 8%
Interval	every 30 reflections
Background	40 second counts
Base length of scan	2.0°
Total number of reflections collected:	2693

The phase problem was solved by the "image seeking" method. A sharpened Patterson synthesis was calculated for the whole cell using 0.6 angström resolution. A distinct pattern of peaks was observed about the origin and in the center of the cell about the threefold axis. The two tetrahedra of cobalt atoms along the threefold axis in $R\bar{3}$ are related by a center of inversion and thus the clusters must be as represented in Figure V-B-2. The pattern of peaks at the origin in the Patterson represents intramolecular vectors (or vectors between identically-oriented molecules). If each atom of cluster 1 is in turn placed on the origin, the pattern shown for the peaks about the Patterson origin is as shown in Figure V-B-2. The sizes of the circles represent the multiplicity of the peaks whereas the sign indicates whether the peak is above or below the plane of the unsigned peaks. The pattern created by cluster 2 reinforces that from cluster 1.

The peaks due to the heavy atoms which are seen in the center of the Patterson map are due to the vectors between cluster 1 and cluster 2. Figure V-B-2 gives the theoretical pattern for 2:1 and 1:2 vectors. These two series of triangles are intermeshed but do not exactly coincide since the centroids of the tetrahedra in the real cell are not exactly at 0.25 and 0.75 of the threefold axis length. The peak marked * was chosen as the $2x_1$, $2y_1$, $2z_1$ peak corresponding to the cobalt atom on

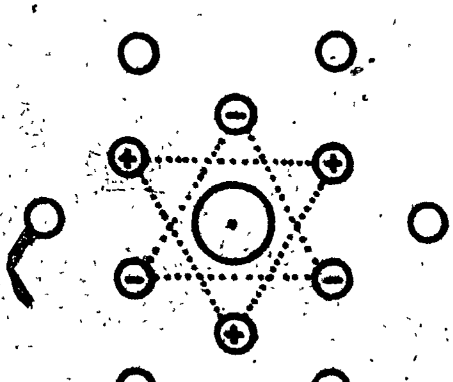
Figure V-B-2. Patterson peaks for the vectors between cobalt atoms in benzeneenneacarbonyltetracobalt(0).



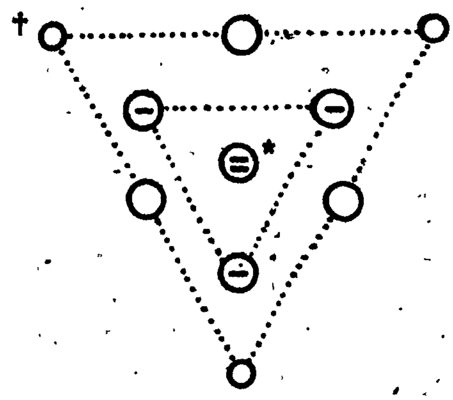


1 2

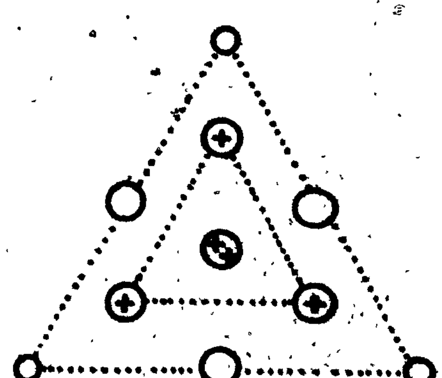
The two tetrahedra



Patterson peaks for
intra-cluster vectors



Patterson peaks for
inter-cluster vectors



the threefold axis whereas that marked † was taken as the $2x_2$, $2y_2$, $2z_2$ peak of the other cobalt atoms ($2y_2$, $2z_2$, $2x_2$ and $2z_2$, $2x_2$, $2y_2$ derived therefrom). In such a manner, cobalt atoms at $2x_1 = 2y_1 = 2z_1 = 0.385$ or 0.192, 0.192, 0.192 and $2x_2 = 0.630$, $2y_2 = 0.385$, $2z_2 = 0.798$ or 0.315, 0.192,0.399 were found.

A structure factor calculation based on the two cobalt atom positions was carried out. The discrepancy factor was 33.9% and the weighted discrepancy factor was 36.8%. An observed Fourier was calculated based on this model. One-third angström resolution showed all the atoms in the molecule and their positions were recorded. With all the atoms included, the residual index was 28.6% for the first complete structure factor calculation. Isotropic thermal parameters *B* were initiated at 2.5 for cobalt atoms, 4.0 for carbon atoms and 5.0 for the carbonyl oxygens. These were allowed to refine along with the positional parameters. After three isotropic refinement cycles, convergence gave a residual index of 8.5% whereas the weighted residual index was 8.0%. All the parameters seemed well-behaved. A summary of the progress of least squares refinement can be found in Table V-B-10.

Before continuing with anisotropic refinement, it was deemed wise to merge the data since redundant reflections had been collected. A computer program was written

TABLE V-B-10

STRUCTURE FACTOR INFORMATION FOR BENZENEENNEACARBONYLTETRACOBALT(0)[a]

	BEFORE REFINE-MENT	ISO(1)	ISO(2)	ISO(3)	ANISO (1)[b]	ANISO (2)
Scale Factor	0.8100	0.8423	0.8615	0.8756	0.8710	0.8702
Number of Matrices		1	1	1	1	1
Total # of Parameters		39	39	39	85	85
Number of Reflections	1964	1964	1964	1964	491	491
"Goodness of fit"	7.420	2.579	2.533	2.540	1.462	1.245
R	28.6	10.8	10.6	8.5	3.4	3.3
R_w	30.2	10.5	10.3	8.0	3.2	3.0

a The structure factor calculation data listed is for that run immediately AFTER the least squares refinement cycle heading the column.

b Results for the merged data (see text).

and the data were merged as follows. Reflections were read into an array bounded by maximum and minimum values of the observed h, k and l indices. The program then generated values of these indices (l changing most rapidly) in decreasing values of h, k and l and the array was searched for symmetry-related reflections (hkl, lhk, klh, $-h-k-l$, $-l-h-k$, $-k-l-h$). Those reflections that were present were averaged and labelled with the generated indices.

Anisotropic refinement converged in two cycles with 491 reflections and 85 refined parameters to a discrepancy factor of 3.0%. The 'goodness-of-fit' parameter was 1.245 and although a rejection criterion was introduced such that all reflections for which $(|F_{obs} - F_{cal}|/F_{obs})$ was greater than 0.5 should not be used in refinement, no reflections were so affected. Anomalous dispersion corrections were applied for the cobalt atoms ($\Delta f' = 0.4$, $\Delta f'' = 1.1$).

Appendix E contains a list of observed and calculated structure factors for the 491 reflections used in the refinement. Also listed are the positional parameters and the thermal parameters for the 12 unique atoms. The hydrogen atom positions were calculated and used in the structure factor calculations although they were not found on the final difference Fourier map (maximum peak of 0.6 $\Delta e Å^{-3}$).

SECTION C. RESULTS AND DISCUSSION

1. Non-crystallographic

The synthesis of the first π arene-enneacarbonyltetracobalt(0) to take place in this laboratory was purely accidental. From a scientific point of view, this fact is difficult to concede. However, from a pedagogical viewpoint, the experience has been very enriching. Repeating a routine reported procedure for the preparation of π-ditertiarybutylacetylenehexacarbonyldicobalt from dicobaltoctacarbonyl and ditertiarybutylacetylene, an additional step was taken; the reaction mixture, after reaction had occurred, was concentrated and chromatographed on a silica gel column.

The large red product band was eluted first. This was the only band expected but a second olive-green much smaller one remained on the column. There was a hope that this might turn out to be an intermediate in the cyclic trimerization of substituted acetylene (see Section A, Part 4) since the literature report being repeated eventually led to the preparation of 1,2,4-tritertiarybutylbenzene.

The olive-green complex was finally identified as xyleneenneacarbonyltetracobalt(0). The chemical origin of the xylene was then investigated. After breaking just about every chemical rule to attempt a rationalization of the mechanism of formation of xylene from ditertiarybutylacetylene, it was decided to investigate the experimental parameters. Hexane (supplied by ANACHEMIA and a product of their solvent extraction process) was used for this reaction. It had been previously dried and distilled before use but a considerable quantity of xylene remained present as an impurity. Although this was not proven directly, when the reaction sequence was repeated using this hexane treated to destroy all aromatic impurities, no olive-green product was recovered. The ditertiarybutylacetylene was not involved in the formation of the xylene complex since, when $Co_2(CO)_8$ was heated in the untreated hexane, the olive-green product was again present.

The mass spectrum of xyleneenneacarbonyltetracobalt(0) shows two principal peaks just as does the spectrum of pure xylene (whether it be *ortho*-, *meta*- or *para*-).[393] This is not altogether surprising since one would intuitively expect the π bonded xylene moiety to separate very readily (m/e 106; $C_8H_{10}^+$) from the rest of the molecule. The second peak at m/e 91 probably results from the loss of one CH_3 resulting in the species $C_7H_7^+$.

Other π arene complexes were synthesized using tetracobaltdodecacarbonyl ($Co_4(CO)_{12}$) as a precursor. Although most of the complexes synthesized have been previously reported, hexafluorobenzene- and hexachlorobenzeneenneacarbonyltetracobalt(0) are novel. If the percentage yields of these reactions with various arenes are examined, it is noted that the yield increases with increasing electron donating ability of the arene. Thus, the halogen-substituted benzene complexes (especially fluorine which is very electronegative) are produced in low yield. As a greater number of methyl groups are substituted onto the ring, the electron donating ability of the arene increases and so does the yield. The yields of the complexes are in the arene order hexamethylbenzene (89.2%) > mesitylene (78.9%) > xylene (average 44.2%) > benzene (38.6%) > hexachlorobenzene (31.4%) > hexafluorobenzene (3.1%). The actual percentage yields should not be quantitatively compared but, from a qualitative point of view, the evidence seems sound.

The electron releasing ability of the arene is also reflected in the decomposition ranges for the complexes which vary from 143-145^{o} for the perfluorobenzene complex to 162-165^{o} for the hexamethylbenzene complex. Decomposition occurred first with liberation of the free arene and sublimation of $Co_4(CO)_{12}$ crystals. A cobalt metallic mirror and a black powder remained in the capilliary tube after decomposition. Since decomposition temperature here reflects the strength of the cobalt-arene bond(s), the observed trends are expected.

The arene complexes were also synthesized thermally from $Co_2(CO)_8$. However, the reaction was allowed to proceed for 36 hours rather than 26 hours for the reactions with $Co_4(CO)_{12}$ precursors. It surely must be a reflection on the lack of thoroughness of past chemical practice that π-areneenneacarbonyltetracobalt(0) complexes were only first reported in late 1971.[387] With benzene as such a common solvent and with so many attempted reactions of $Co_2(CO)_8$, simple chromatographic practice should have led to the discovery of $(C_6H_6)Co_4(CO)_9$. It might also be a reflection on the degree of reactivity of $Co_2(CO)_8$ with most ligands used that such a complex was never isolated.

It is interesting to note that the percentage yields of the various π-areneenneacarbonyltetracobalt complexes are essentially the same, regardless of the precursor ($Co_4(CO)_{12}$: Table V-B-3 and $Co_2(CO)_8$: Table V-B-4). This, coupled with the fact that $Co_4(CO)_{12}$ is recovered from the $Co_2(CO)_8$ reactions, implies that the formation of the arene complex from $Co_2(CO)_8$ is likely to involve $Co_4(CO)_{12}$ as an intermediate. This last species might subsequently lose 3 carbonyl ligands which are replaced by the arene as in a proposed reaction sequence involving $Co_4(CO)_{12}$ as a starting material. The formation of $Co_4(CO)_{12}$ from $Co_2(CO)_8$ has been described by Ungváry and Markó[26] and is believed to proceed *via* a $Co_2(CO)_6$ intermediate.

The π-areneenneacarbonyltetracobalt complexes all display similar carbonyl stretching bands in the infrared (see Figure V-B-1). These bands are so characteristic that full chemical analyses were deemed unnecessary for every (arene)$Co_4(CO)_9$ complex synthesized. Only the benzene and hexamethylbenzene complexes were subjected to chemical analysis. The four terminal carbonyl bands are listed in Table V-B-5 for the seven complexes reported. Not only are the terminal carbonyl frequencies shifted from their values in $Co_4(CO)_{12}$ but a change of approximately 40 cm^{-1} exists between the parent $Co_4(CO)_{12}$ and the arene complex in the bridging carbonyl stretching frequency.

The difference between $Co_4(CO)_{12}$ and (arene)·$Co_4(CO)_9$ lies in the substituents on the apical cobalt atom. In the former complex, three carbonyl ligands are present whereas in the latter, these carbonyls are replaced by an arene. Since the three carbonyls are more electron withdrawing (better π acceptors) than the arene, electron density is pulled from the cobalt-carbon (bridging carbonyl) bond. This decreases the extent of back donation from the metal into the π^* orbital of the carbon and thus increases the strength of the C–O bridging carbonyl bond as compared to (arene)$Co_4(CO)_9$. This explains why the stretching frequency mainly associated with this bond is at 1860 cm^{-1} for $Co_4(CO)_{12}$ and at approximately 1820 cm^{-1} for the (arene)$Co_4(CO)_9$ complex.

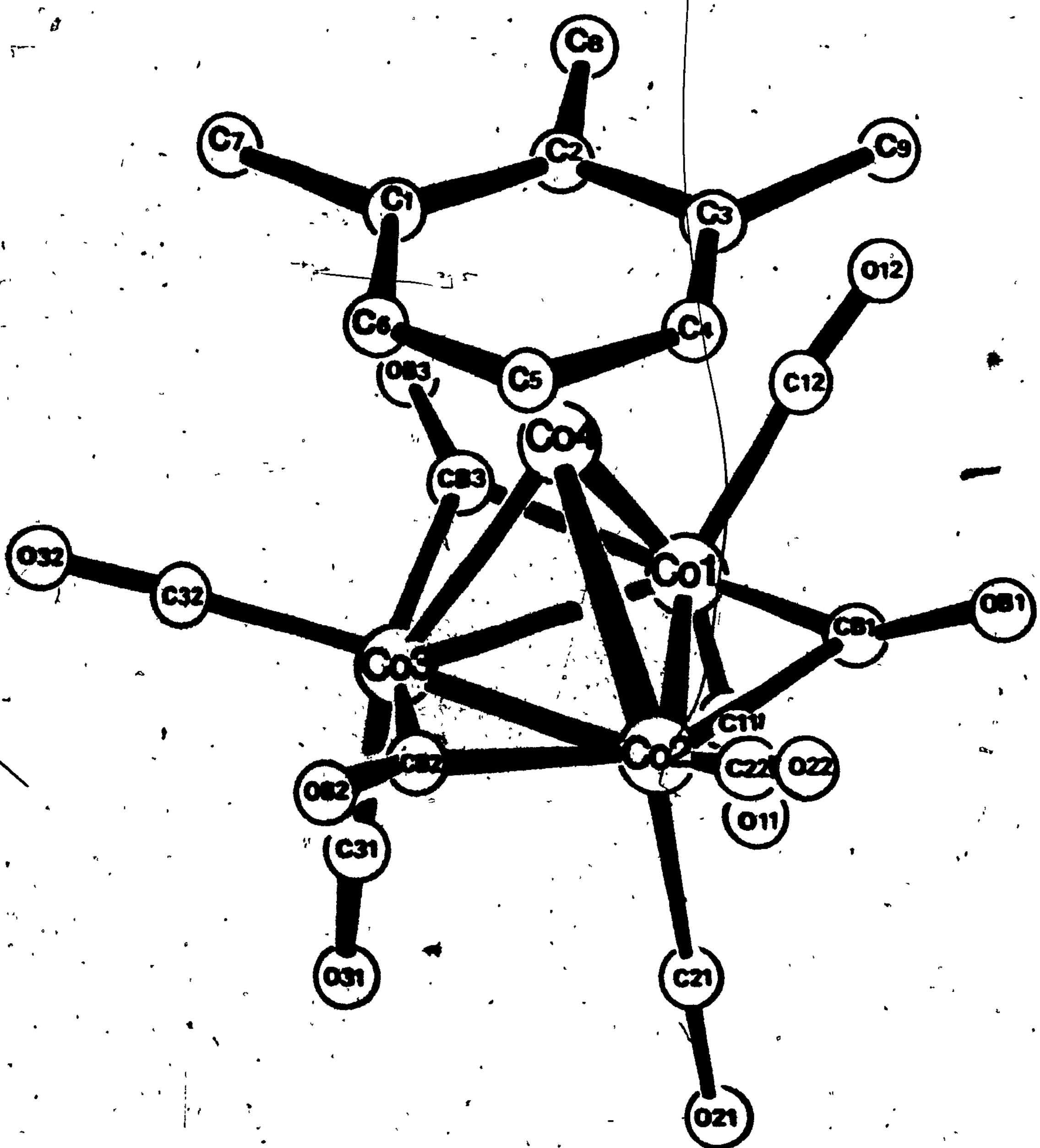
It would have been informative to study the precise terminal and bridging carbonyl frequencies for all the arene $Co_4(CO)_9$ complexes in order to attempt a correlation between the electron releasing nature of the arene substituents and the carbonyl stretching frequencies. This type of study has been accomplished for $PhCCo_3(CO)_6$(arene)[370] (see Table V-A-4) with the expected result that the more electron releasing the substituent, the lower the stretching frequency in the infrared.

2. The Crystal and Molecular Structure of the Disordered *ortho*- and *meta*-xyleneenneacarbonyltetracobalt Complex

The crystal structure shows discrete molecules of xyleneenneacarbonyltetracobalt as described in Figure V-C-1. The structure can be considered derived from the $Co_4(CO)_{12}$ structure (Figure I-2) by replacement of the three terminal carbonyls on the apical cobalt atom of the tetrahedron of cobalt atoms by a π bonded arene. The three basal cobalt atoms are bonded just as in $Co_4(CO)_{12}$: three equivalent $Co(CO)_2$ groups bonded by both Co-Co bonds and single bridging carbonyl ligands. There appears to be no significant deviation from three-fold symmetry of the $Co_4(CO)_9$ entity.

The xylene moiety is a 1:1 mixture of *o*-xylene and *m*-xylene in which one crystallographic site is occupied by methyl groups of both isomers whereas the other two

Figure V-C-1. The molecular configuration for xyleneenneacarbonyltetracobalt. The numbering scheme is the same for benzeneenneacarbonyltetracobalt.


C8
C7
C2
C9
C1
C3
O12
C6
C4
OB3
C5
C12
Co4
CB3
O32
Co1
C32
OB1
CB1
Co3
C11
Co2
C22
O22
CB2
OB2
O11
C31
O31
C21
O21

crystallographic sites exhibit half occupancy. When the packing forces are described, an explanation of the mixed crystal character will be attempted. The full occupancy methyl carbon peak was refined anisotropically but the half carbon atoms were not so refined. The crystallographic positions of the disordered groups are not very precise but they have been included in the tables describing the geometry of the molecule.

The bond lengths in the xyleneenneacarbonyltetracobalt(0) complex as determined by this X-ray crystallographic study are given in Table V-C-1. The angles between these bonds are shown in Table V-C-2. The numbering scheme used is that shown in Figure V-C-1. This view of the molecule is down the *c* axis of the monoclinic cell. The average basal-to-apical cobalt atom distance is 2.480(6)Å whereas the average basal Co-Co distance is 2.454(2)Å. Although this difference is small, it could be ascribed to the presence of bridging carbonyl ligands in the latter case but not in the former. Differences of this type are usually larger (0.06 - 0.10Å) as reported by Chini,[24] but in $Co_4(CO)_{12}$ they were found to be statistically non-valid. It should be pointed out that this last structure is very badly disordered so that differences of this type might remain undetected.

The Co-Co distances are not at all unusual, falling as they do within the range found for the Co-Co

TABLE V-C-1

BOND LENGTHS (Å) IN XYLENEENNEACARBONYLTETRACOBALT

Co1-Co4: 2.491(2)	Co2-Co4: 2.477(2)	Co3-Co4: 2.472(2)
Co1-Co2: 2.456(2)	Co2-Co3: 2.451(2)	Co3-Co1: 2.456(2)
Co1-C11: 1.772(13)	Co2-C21: 1.774(11)	Co3-C31: 1.783(12)
Co1-C12: 1.794(12)	Co2-C22: 1.800(13)	Co3-C32: 1.763(13)
Co1-CB3: 1.938(12)	Co2-CB1: 1.946(11)	Co3-CB2: 1.949(11)
Co1-CB1: 1.865(12)	Co2-CB2: 1.911(10)	Co3-CB3: 1.926(12)
C11-O11: 1.154(17)	C21-O21: 1.152(14)	C31-O31: 1.150(16)
C12-O12: 1.134(14)	C22-O22: 1.122(16)	C32-O32: 1.155(16)
CB1-OB1: 1.194(15)	CB2-OB2: 1.178(12)	CB3-OB3: 1.161(16)
Co4-C1 : 2.195(11)	Co4-C3 : 2.141(13)	Co4-C5 : 2.178(14)
Co4-C2 : 2.132(12)	Co4-C4 : 2.147(15)	Co4-C6 : 2.171(12)
C1 -C2 : 1.436(17)	C3 -C4 : 1.373(21)	C5 -C6 : 1.391(19)
C2 -C3 : 1.452(21)	C4 -C5 : 1.413(22)	C6 -C1 : 1.402(18)
C1 -C7 : 1.533(20)	C2 -C8 : 1.377(37)	C3 -C9 : 1.477(44)

TABLE V-C-2

BOND ANGLES (°) IN XYLENEENNEACARBONYLTETRACOBALT(0)

Co1-Co4-Co2:	59.27(5)	Co2-Co4-Co3:	59.38(5)	Co3-Co4-Co1:	59.33(5)
Co4-Co1-Co2:	60.08(5)	Co4-Co2-Co3:	60.22(5)	Co4-Co3-Co1:	60.71(5)
Co4-Co1-Co3:	59.96(5)	Co4-Co2-Co1:	60.65(5)	Co4-Co3-Co2:	60.40(5)
Co4-Co1-CB3:	73.3(4)	Co4-Co2-CB1:	78.0(4)	Co4-Co3-CB2:	73.9(4)
Co4-Co1-C12:	99.2(4)	Co4-Co2-C22:	97.9(4)	Co4-Co3-C32:	101.9(4)
Co4-Co1-CB1:	79.1(4)	Co4-Co2-CB2:	74.4(3)	Co4-Co3-CB3:	74.0(4)
Co4-Co1-C11:	162.8(4)	Co4-Co2-C21:	161.6(4)	Co4-Co3-C31:	158.7(4)
Co3-Co1-CB3:	50.3(4)	Co1-Co2-CB1:	48.4(3)	Co2-Co3-CB2:	49.9(3)
Co3-Co1-C12:	141.4(4)	Co1-Co2-C22:	138.4(4)	Co2-Co3-C32:	141.1(4)
Co3-Co1-CB1:	110.7(3)	Co1-Co2-CB2:	109.9(4)	Co2-Co3-CB3:	109.1(4)
Co3-Co1-Co2:	59.86(5)	Co1-Co2-Co3:	60.06(5)	Co2-Co3-Co1:	60.07(5)
CB3-Co1-C12:	94.3(5)	CB1-Co2-C22:	94.8(5)	CB2-Co3-C32:	93.3(5)
CB3-Co1-CB1:	152.0(5)	CB1-Co2-CB2:	151.6(5)	CB2-Co3-CB3:	147.7(5)
CB3-Co1-Co2:	108.5(4)	CB1-Co2-Co3:	108.0(4)	CB2-Co3-Co1:	108.5(4)

TABLE V-C-2 (CONT'D)

C12-Co1-CB1:	94.7(5)	C22-Co2-CB2:	95.7(4)	C32-Co3-CB3:	96.6(5)
C12-Co1-Co2:	140.9(4)	C22-Co2-Co3:	142.7(4)	C32-Co3-Co1:	144.9(4)
CB1-Co1-Co2:	51.3(3)	CB2-Co2-Co3:	51.3(3)	CB3-Co3-Co1:	50.8(4)
C11-Co1-Co3:	104.0(4)	C21-Co2-Co1:	104.9(4)	C31-Co3-Co2:	101.3(4)
C11-Co1-CB3:	102.0(5)	C21-Co2-CB1:	101.2(5)	C31-Co3-CB2:	103.4(5)
C11-Co1-C12:	97.7(5)	C21-Co2-C22:	100.4(5)	C31-Co3-C32:	99.3(6)
C11-Co1-CB1:	102.9(5)	C21-Co2-CB2:	102.7(5)	C31-Co3-CB3:	105.1(5)
C11-Co1-Co2:	107.5(4)	C21-Co2-Co3:	103.5(4)	C31-Co3-Co1:	101.7(4)
Co1-C11-O11:	177(1)	Co2-C21-O21:	178(1)	Co3-C31-O31:	175(1)
Co1-C12-O12:	179(1)	Co2-C22-O22:	178(1)	Co3-C32-O32:	176(1)
Co1-CB3-OB3:	139(1)	Co2-CB1-OB1:	135(1)	Co3-CB2-OB2:	138(1)
Co1-CB1-OB1:	144(1)	Co2-CB2-OB2:	143(1)	Co3-CB3-OB3:	142(1)
Co1-CB1-Co2:	80.2(4)	Co2-CB2-Co3:	78.8(4)	Co3-CB3-Co1:	78.9(5)

TABLE V-C-2 (CONT'D)

Co1-Co4-C1 :	131.6(4)	Co2-Co4-C1 :	159.9(3)	Co3-Co4-C1 :	108.8(3)
Co1-Co4-C2 :	109.2(4)	Co2-Co4-C2 :	161.4(3)	Co3-Co4-C2 :	130.1(4)
Co1-Co4-C3 :	109.6(4)	Co2-Co4-C3 :	126.5(4)	Co3-Co4-C3 :	164.5(4)
Co1-Co4-C4 :	128.4(4)	Co2-Co4-C4 :	104.5(4)	Co3-Co4-C4 :	157.8(4)
Co1-Co4-C5 :	160.0(4)	Co2-Co4-C5 :	105.5(4)	Co3-Co4-C5 :	126.7(4)
Co1-Co4-C6 :	161.8(3)	Co2-Co4-C6 :	126.3(3)	Co3-Co4-C6 :	106.8(3)
C6 -C1 -C2 :	120(1)	C2 -C3 -C4 :	121(1)	C4 -C5 -C6 :	121(1)
C1 -C2 -C3 :	118(1)	C3 -C4 -C5 :	119(2)	C5 -C6 -C1 :	120(1)
C6 -C1 -C7 :	121(1)	C1 -C2 -C8 :	122(2)	C2 -C3 -C9 :	113(2)
C2 -C1 -C7 :	119(1)	C3 -C2 -C8 :	120(2)	C4 -C3 -C9 :	126(2)

bond in various cobalt cluster complexes (2.43 - 2.64Å).[394] In xyleneenneacarbonyltetracobalt, the average C–O terminal carbonyl distance is $1.14^{4}(0^{5})$ Å. The average C–O bridging carbonyl is longer ($1.17^{8}(0^{9})$ Å) although caution must be exercised in comparing carbonyl bond lengths. Both values are within the ranges quoted by Chini[24] (terminal: 1.12-1.19Å, edge bridging: 1.165 - 1.20Å). The average Co–C (bridging carbonyl) distance is $1.92^{3}(1^{3})$Å. The average Co–C (basal terminal carbonyl (C11,C21,C31)) is not significantly different from the average Co–C (equitorial terminal carbonyl (C12,C22,C32)) distance. Values of $1.77^{6}(0^{3})$ and $1.78^{6}(1^{1})$ respectively are quite normal.

Although comparison with a disordered structure such as $Co_4(CO)_{12}$ is undoubtedly not valid, especially where carbonyl bond distances are concerned, comparison of certain average bond lengths is tempting. For $Co_4(CO)_{12}$, the average terminal C≡O and bridging C–O distances are 1.02Å and 1.16Å respectively and the average Co–C (terminal carbonyl) and Co–C (bridging carbonyl) bond lengths are 1.84Å and 2.06Å respectively. When compared to the related average distances in (xylene)$Co_4(CO)_9$, it is found that the C-O distances are shorter and the Co-C distances are longer in $Co_4(CO)_{12}$. Viewing the metal tetrahedron as a single metallic entity, the above trends can be explained in terms of the better π acceptor quality of three carbonyls (in $Co_4(CO)_{12}$) when compared to an arene. Less electronic charge is thus available for Co-C bonding (thus a longer bond). Since the C-O bond length partly depends upon the electronic charge available for back donation from the metal to the antibonding carbon orbital, the $Co_4(CO)_{12}$ C≡O bonds can be expected to be shorter. This is in point of fact observed although, as stated above, these conclusions should be viewed with considerable skepticism. Since the carbonyl carbon position is notoriously unreliable, and since it is used to calculate both Co-C and C-O distances from which these arguments are derived, one should be doubly cautious.

There are no outstanding anomalies in the bond angles for the complex. The average cobalt tetrahedron angle is 60.0° but the average Co-Co-Co angle at the apex of the tetrahedron is 0.6° smaller than that for metal angles about the base. This reflects the difference in the Co-Co bond lengths, the base-to-apex bonds being longer than those bonds between basal cobalts.

The Co-Co-C ring for the bridging carbonyl forms an angle of 13.7(5)° with the basal Co-Co-Co ring. The carbon atom is at an average of 0.35Å above the Co-Co-Co plane (toward the apical cobalt). The oxygen of the bridging carbonyl is in the plane of the Co-Co-C ring (within 2°). The bridging carbonyl Co-C-Co angle averages 79.1° which is at the extreme low end of the range of edge M-C-M angles quoted by Chini (79-87°).[24] The bridging carbonyl is only very slightly disymmetric with Co1-CB3, Co3-CB2 and Co2-CB1 lengths averaging 1.94^{4}(0^{3})Å and Co1-CB1, Co2-CB2 and Co3-CB3 bond lengths averaging 1.90^{1}(1^{8})Å. Such a phenomenon has the effect of giving a degree of terminal character to the bridging carbonyls. The carbonyl can be considered associated more strongly with the closest cobalt atom (CB1 with Co1, CB2 with Co2 and CB3 with Co3).

This behaviour has been observed before in the case of the ion $(Fe_4(CO)_{13})^{2-}$ [395] which consists of a tetrahedral framework of iron atoms with twelve carbonyls distributed as in $Co_4(CO)_{12}$ and the thirteenth carbonyl triply bridging the three basal iron atoms. The Fe-C bond differences for the edge bridging carbonyls in this complex were much larger (>0.4Å) than in (xylene)$Co_4(CO)_9$. In the complex di-μ-{1,2-bis(dimethylarsino)tetrafluorocyclobutene}-octacarbonyl-*tetrahedro*-tetracobalt [177] discussed in Chapter IV, Section A of this Thesis, a tetrahedron of cobalt atoms is bridged by two 1,2-bis(dimethylarsino)tetrafluorocyclobutene ligands. Each cobalt has two 'terminal' carbonyl ligands associated with it. One is, for all intents and purposes, linear but the second is bent in an attempt to bridge. Both these examples describe a tendency for bridging carbonyls to become terminal perhaps due to the high degree of strain associated with small interatomic angles. The trends in the (arene)$Co_4(CO)_9$ complexes studied here are only hints of this type of distortion.

A similar argument has been made [396] for the non-linear terminal carbonyl M-C-O angle which, for (xylene)$Co_4(CO)_9$, averages 177°. Here, the π bonding is of somewhat different strength in the two mutually perpendicular directions.

The final thermal parameters were used to compute the major, median and minor axes of the thermal vibration ellipsoids for the individual atoms and their direction cosines. The axis lengths are in units of B where the root mean square displacement $(\bar{U}^2)^{\frac{1}{2}} = (B/8\pi^2)^{\frac{1}{2}}$ and these values are quoted in Table V-C-3. The molecule, as viewed in Figure V-C-1, is reproduced in Figure V-C-2. Here, the 68% probability envelopes of the vibration ellipsoids are shown for the atoms in the molecule. The dotted bonds and circles represent the two disordered methyl groups. All features of thermal vibration of the atoms in (xylene)$Co_4(CO)_9$ appear to be normal.

The planes described by Co1-Co2-Co3, CB1-CB2-CB3 and OB1-OB2-OB3 are all parallel (within 2°). However, the least squares plane to the six benzenoid carbon atoms is tilted 2.6° with respect to these aforementioned planes. This tilt can be seen by examining the apical cobalt-to-ring carbon distances quoted in Table V-C-1, the corresponding angles in Table V-C-2 and, most clearly, by Figure V-C-3 which is a projection down the *pseudo* three-fold axis of the molecule.

TABLE V-C-3

THERMAL VIBRATION ELLIPSOIDS[a]- XYLENEENNEACARBONYLTETRACOBALT

Atom	Axes[b]	Direction Cosines		
Co1	4.35	0.53803	0.20287	0.81814
	3.42	0.83880	-.03303	-.54344
	2.53	0.08318	-.97865	0.18794
Co2	4.08	-.07059	0.00535	0.99749
	3.77	0.80665	0.58861	0.05392
	2.52	0.58688	-.80840	0.04586
Co3	4.06	0.58534	-.02876	0.81027
	3.64	0.80863	-.05218	-.58601
	2.48	0.05909	0.99822	-.00729
Co4	4.46	0.28616	-.21090	0.93468
	3.88	0.78142	0.61593	-.10026
	2.31	0.55459	-.75904	-.34106
C1	8.97	0.15886	-.49871	0.85208
	4.00	0.66699	0.69051	0.27977
	2.29	0.72792	-.52391	-.44237
C2	6.81	0.76950	0.63721	0.04337
	6.14	0.08067	-.16434	0.98310
	2.65	0.63360	-.75297	-.17787
C3	11.97	0.35159	-.31076	0.88306
	5.68	0.90172	0.36594	-.23026
	2.22	0.25163	-.87722	-.40888
C4	9.29	0.27020	0.77821	-.56692
	6.80	0.73040	0.21798	0.64729
	2.83	0.62734	-.58896	-.50953
C5	9.18	0.54739	-.35820	0.75633
	7.03	0.43305	0.89459	0.11020
	2.39	0.71610	-.26722	-.64484
C6	7.87	0.60126	0.77852	-.18012
	4.99	0.51034	-.20065	0.83623
	3.14	0.61491	-.59468	-.51795
C7	12.43	0.17168	0.57378	-.80082
	7.88	0.16731	-.81806	-.55027
	3.94	0.97085	0.03950	0.23640
C11	8.70	0.64772	0.19713	0.73593
	5.18	0.66180	-.62420	-.41526
	2.50	0.37754	0.75599	-.53477

TABLE V-C-3 (CONT'D)

O11	18.30	0.77308	-.13999	0.61866
	7.32	0.29992	0.94013	-.16198
	4.13	0.55896	-.31074	-.76878
C12	5.70	0.69010	0.46989	0.55040
	5.38	0.71844	-.35317	-.59929
	2.92	0.08717	-.80900	0.59131
O12	11.91	0.43845	0.41852	0.79535
	7.97	0.89605	-.13494	-.42297
	3.76	0.06966	-.89813	0.43418
CB1	6.59	0.95875	0.15408	0.23882
	6.18	0.28227	-.41781	-.86358
	2.44	0.03334	-.89537	0.44407
OB1	13.70	0.56785	-.31778	-.75933
	6.98	0.59742	-.47545	-.64576
	3.54	0.56619	0.82035	0.08012
C21	6.03	0.10492	-.50024	-.85951
	4.61	0.37571	-.78028	0.49998
	2.79	0.92078	0.37541	-.10612
O21	8.52	0.23561	0.28268	0.92982
	7.90	0.31349	0.88353	-.34803
	4.28	0.91993	-.37346	-.11958
C22	7.90	0.64855	0.07223	-.75774
	4.68	0.68646	0.37456	0.62326
	3.83	0.32879	-.92339	0.19334
O22	15.06	0.73011	0.46973	-.49632
	6.77	0.52065	-.85280	-.04130
	4.44	0.44265	0.22823	0.86716
CB2	6.44	-.04303	0.18757	0.98108
	4.17	0.33183	0.92943	-.16145
	2.59	0.94215	-.31775	-.10687
OB2	8.17	0.02755	0.73193	0.68082
	7.32	0.97052	-.18372	0.15711
	3.25	0.23943	0.65643	-.71740
C31	6.77	0.98090	0.11487	0.15692
	5.04	0.01076	-.83784	0.54580
	3.46	0.19420	-.53369	-.82309
O31	11.78	0.12310	0.57346	-.80994
	11.16	0.96090	0.13510	0.24166
	3.13	0.24804	-.80802	-.53442

TABLE V-C-3 (CONT'D)

C32	6.32	0.95030	0.09054	0.29788
	4.99	0.31105	-.23410	-.92112
	3.04	0.01362	-.96799	0.25062
O32	9.42	0.46405	-.22371	0.85709
	8.83	0.41557	-.79954	-.43367
	3.54	0.78232	0.55739	-.27808
CB3	6.13	0.64552	0.06715	0.76078
	5.30	0.72971	-.34835	-.58829
	2.96	0.22555	0.93496	-.27387
OB3	14.93	0.50091	-.54263	-.67429
	5.72	0.67808	0.73021	-.08397
	3.49	0.53792	-.41554	0.73367

[a] Given in the order of major, median and minor axes.

[b] Axis lengths are in units of B where the root mean square displacement $(\bar{U}^2)^{\frac{1}{2}} = (B/8\pi^2)^{\frac{1}{2}}$.

Figure V-C-2. A projection down the *c* axis showing the 68% probability ellipsoids for xyleneenneacarbonyltetracobalt(0).

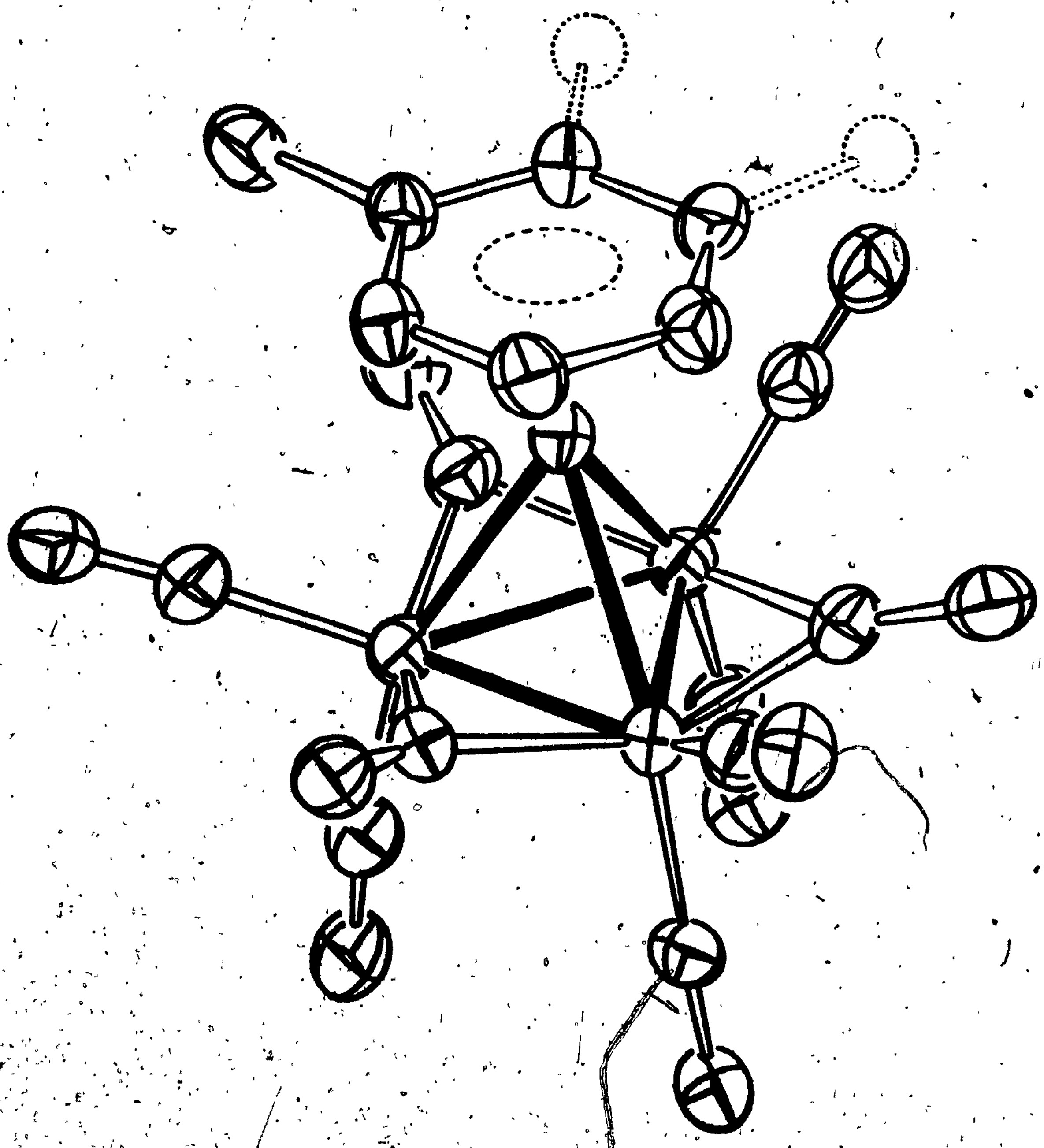
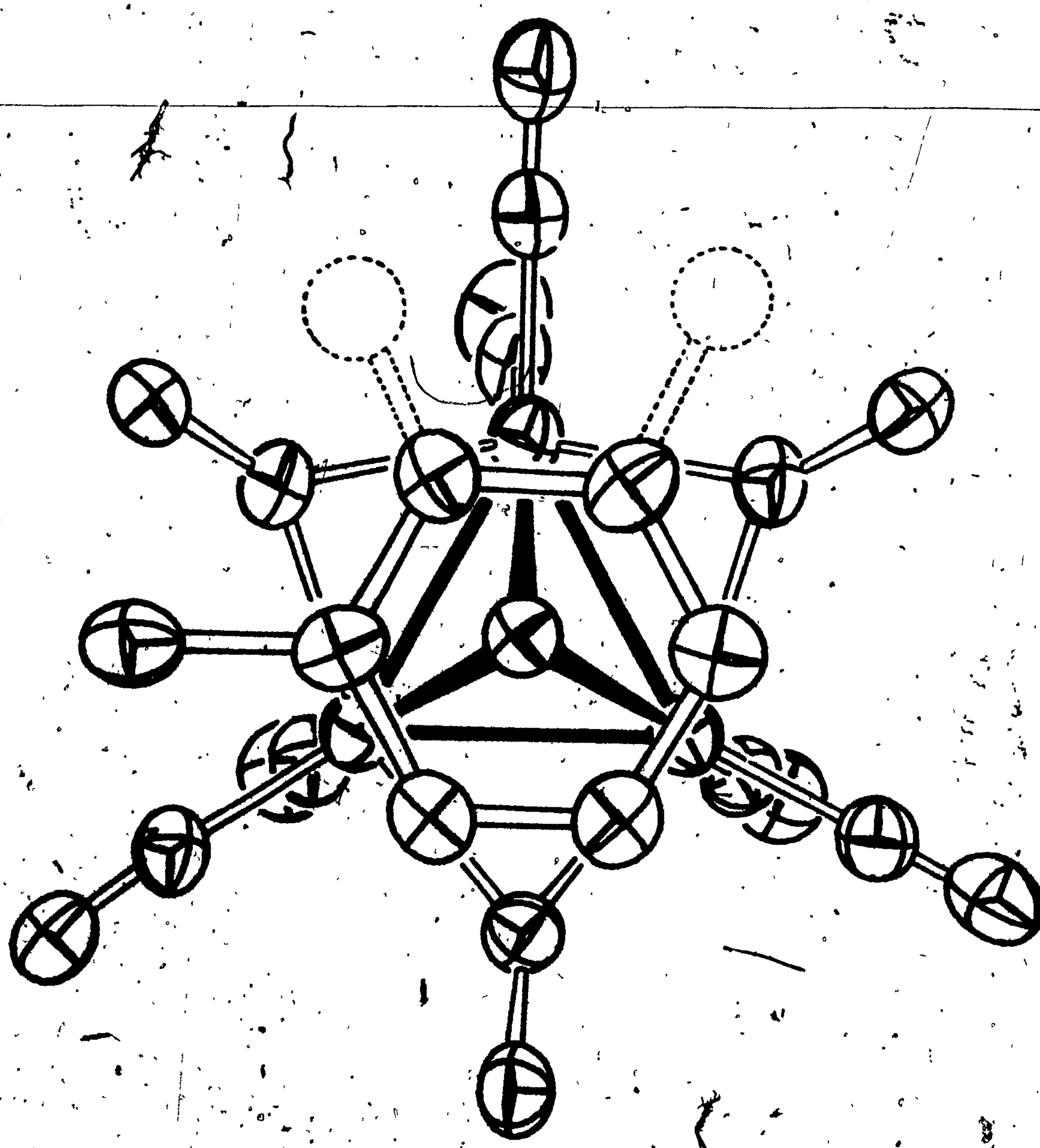


Figure V-C-3. A projection down the *pseudo* three-fold axis showing the 68% probability ellipsoids for xyleneenneacarbonyltetracobalt(0).



It will be noted that the carbons closest to Co4 are those that are substituted. This suggests that steric interactions are unlikely to be responsible for this trend.

Table V-C-4 gives all the non-bonded intramolecular contacts in the (xylene)$Co_4(CO)_9$ disordered molecule to 3.0Å. It is obvious from a study of this table that these contacts play no role in influencing the direction of tilt of the benzenoid plane. Another tempting explanation is that there is a degree of localized bonding of the arene to the transition metal atom. Since the ring is disordered, the importance of certain anomalies must be kept in perspective. Some or all of the trends observed may be artifacts but it was considered they were worthy of mention.

Since bond C2 - C3 is closest to the cobalt atom, perhaps a larger contribution of the π bond is due to this interaction rather than the others. If this were so, this bond length would be longer than the others since π electron density is taken principly from this bond. This is in fact observed (1.452(21)Å) although the differences are not very statistically significant. According to the χ^2 distribution, there is but a 5% probability that the six C - C bond lengths in the benzenoid ring are identical provided the estimated standard deviations truly reflect the deviations of the bonds.

TABLE V-C-4

NON-BONDED INTRAMOLECULAR CONTACTS (Å) FOR (XYLENE)$Co_4(CO)_9$[a,b]

C11-CB3:	2.89	C21-CB1:	2.88	C31-CB2:	2.93
C11-CB1:	2.84	C21-CB2:	2.88	C31-CB3:	2.95
C11-C12:	2.68	C21-C22:	2.75	C31-C32:	2.70
C12-CB3:	2.74	C22-CB1:	2.76	C32-CB2:	2.70
C12-CB1:	2.69	C22-OB2:	2.75	C32-CB3:	2.76
Co4-CB3:	2.68	Co4-CB1:	2.82	Co4-CB2:	2.69
Co4-H4 :	2.86	Co4-H5 :	2.94	Co4-H6 :	2.88
		Co4-H4 :	2.86	Co4-H6 :	2.88
C7 -C8 :	2.91	C8 -C9 :	2.73		

a Only those atomic contacts less that 3.0Å are quoted.

b Intra-ring distances are not listed except for methyl-methyl carbon distances.

There is in fact a hint of an alteration of bond lengths about the benzenoid ring (1.436(17), 1.452(21), 1.373(21), 1.413(22), 1.391(19), 1.402(18)Å) as has been observed for some structures reported in the Introduction of this Chapter. The least squares plane of the benzenoid ring carbon atoms is 1.64(1)Å above the apical cobalt atom. The deviations (in angströms) from this least squares plane of the individual atoms are 0.02^7, -0.02^4, 0.01^7, -0.01^1, 0.01^4 and -0.02^2. The average C-C bond length in the ring is 1.41(1)Å, somewhat longer than in free xylene (not within estimated standard deviations). Generally, bond lengths of this order are observed for π arene complexes and this reflects a slight decrease in π bonding character of the ring due to the metal atom.

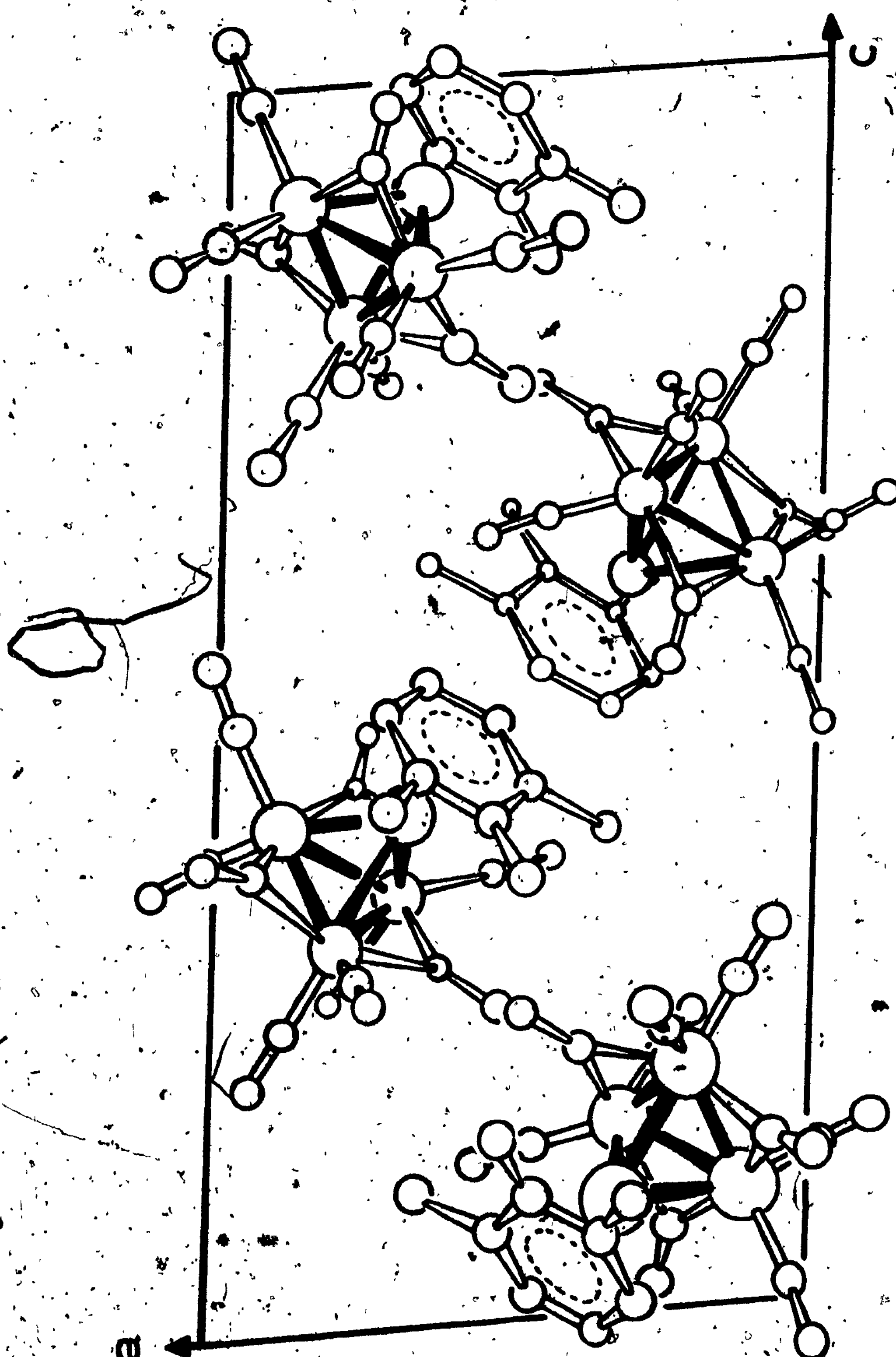
Another fact which is worthy of note is that the Co-Co bonds *trans* to the methyl substituted portions of the arene are shorter (2.477(2) and 2.472(2)Å) than the other bond (2.491(2)Å). This difference is greater than 99% significant according to the χ^2 distribution. In polycyclic arene chromium tricarbonyl complexes (Section A, Part 3) the carbonyl carbon atom *trans* to the ring junction is closest to the chromium atom of the three carbonyl carbon atoms. In this class of compound, the arene carbon atoms furthest from the chromium atom are those at the ring junction. This trend is not as obvious in the (xylene)$Co_4(CO)_9$ complex in relation to the methyl substituted portion of the arene.

The most likely explanation for all these anomalies in the arene moiety and its π bonding to the cobalt atom is that they are all artifacts of the disorder. It is unwise to speculate based on such a structure and this is why the benzene complex was studied by X-ray crystallography. Perhaps if the pure *ortho*-xylene complex had been studied, more information could have been obtained. Nevertheless, a final look at the packing of the molecules in the monoclinic cell will help in an understanding of the disorder obtained.

If one were to speculate on the nature of the rhombohedral crystal first investigated, the obvious conclusion would be that the disorder was complete and that all six crystallographic sites corresponding to arene substituents were occupied by methyl groups. Three-fold symmetry would then be achieved and $R\bar{3}$ would be a plausible space group. The crystal studied was monoclinic and the packing of the four molecules in the unit cell is shown in Figure V-C-4 which is a projection down the unique axis. Intermolecular forces are slight and distances less than 3.0Å are listed in Table V-C-5. The principle interaction seems to be of the hydrogen-oxygen type.

A careful examination of the packing diagram shows that substituent protions of the arene are pointed away from each other in all cases, thereby minimizing methyl-methyl interactions. Why the monoclinic polymorph is

Figure V-C-4. A projection down the unique axis of the monoclinic cell showing the four molecules of xyleneenneacarbonyltetracobalt(0).



c
a

TABLE V-C-5

INTERMOLECULAR CONTACTS (Å) FOR (XYLENE)$Co_4(CO)_9$[a,b]

O82-H6	2.95	O32-H5	2.92
O32-H6	2.91		

[a] Only atomic contacts less than 3.0Å are quoted.

[b] The following transformations give the position of the second atom listed relative to the first which has co-ordinates x,y,z listed in Table D-2, Appendix D.

$1-x\ ,\ -y,\ 1-z$

preferred over the rhombohedral polymorph is not clear.

3. The Crystal and Molecular Structure of Benzeneenneacarbonyltetracobalt(0).

The X-ray crystallographic structure investigation of benzeneenneacarbonyltetracobalt(0) showed two discrete molecules, with internal three-fold symmetry, lying on the three-fold axis of space group $R\bar{3}$. This three-fold axis contains 1) the centroid of the benzene ring π bonded to Co4, 2) the apical cobalt (Co4) of a $Co_4(CO)_9$ tetrahedron very similar to that observed in (xylene)$Co_4(CO)_9$ and 3) the centroid of the triangle described by the three basal cobalt atoms of this tetrahedron.

The cobalt carbonyl moiety was almost exactly identical to that for the disordered xylene complex although the results in the benzene compound should probably be considered more reliable. Tables V-C-6 and V-C-7 give the crystallographically independent bond lengths and angles for the benzene complex. The numbering scheme is identical to that for (xylene)$Co_4(CO)_9$ (Figure V-C-1) except that carbons 7, 8 and 9 are, of course, non-existent. To facilitate comparison, Table V-C-8 lists the average important bond lengths for (xylene)$Co_4(CO)_9$ and those for the benzene analog.

TABLE V-C-6

BOND LENGTHS (Å) IN BENZENEENNEACARBONYLTETRACOBALT

Co1-Co4:	2.485(1)
Co1-Co2:	2.457(2)
Co1-C11:	1.771(9)
Co1-C12:	1.795(10)
Co1-CB3:	1.956(9)
Co1-CB1:	1.939(9)
C11-O11:	1.160(12)
C12-O12:	1.120(12)
CB1-OB1:	1.148(11)
Co4-C1 :	2.122(10)
Co4-C2 :	2.122(13)
C1 -C2 :	1.387(18)
C2 -C3 :	1.394(18)

TABLE V-C-7

BOND ANGLES (°) IN BENZENEENNEACARBONYLTETRACOBALT(0)

Co1-Co4-Co2:	59.25(4)	C12-Co1-CB1:	95.4(4)	Co1-Co4-C1 :	129.8(4)
Co4-Co1-Co2:	60.37(4)	C12-Co1-Co2:	142.0(3)	Co1-Co4-C2 :	107.8(3)
Co4-Co1-Co3:	60.37(4)	CB1-Co1-Co2:	51.2(3)	Co1-Co4-C3 :	106.8(4)
Co4-Co1-CB3:	76.7(3)	C11-Co1-Co3:	103.0(3)	Co1-Co4-C4 :	126.8(3)
Co4-Co1-C12:	98.9(3)	C11-Co1-CB3:	99.7(4)	Co1-Co4-C5 :	159.1(4)
Co4-Co1-CB1:	77.0(3)	C11-Co1-C12:	99.6(4)	Co1-Co4-C6 :	162.5(3)
Co4-Co1-C11:	161.3(3)	C11-Co1-CB1:	103.4(4)	C1 -C2 -C3 :	120(1)
Co3-Co1-CB3:	50.6(3)	C11-Co1-Co2:	105.0(3)	C6 -C1 -C2 :	120(1)
Co3-Co1-C12:	140.3(3)	Co1-C11-O11:	177.3(8)		
Co3-Co1-CB1:	110.3(3)	Co1-C12-O12:	178.6(8)		
Co3-Co1-Co2:	60.00(4)				
		Co1-CB3-OB3:	139.3(7)		
CB3-Co1-C12:	93.8(4)	Co1-CB1-OB1:	142.4(7)		
CB3-Co1-CB1:	153.2(4)	Co1-CB1-Co2:	78.2(3)		
CB3-Co1-Co2:	109.7(3)				

TABLE V-C-8

A COMPARISON OF THE PRINCIPAL BOND LENGTHS (Å) FOR $Co_4(CO)_{12}$, $(XYLENE)Co_4(CO)_9$ AND $(BENZENE)Co_4(CO)_9$[a]

Bond	$(XYLENE)Co_4(CO)_9$[b]	$(BENZENE)Co_4(CO)_9$	$Co_4(CO)_{12}$[b]
Apical-to-Basal Cobalt	2.480(6)	2.485(1)	2.494(8)
Basal Co-Co	2.454(2)	2.457(2)	2.485(25)
Co-Basal CO C	1.776(3)	1.771(9)	1.73(3)
Co-Equatorial CO C	1.786(11)	1.795(10)	1.96(17)
Co-Bridging CO C (clockwise)	1.944(3)	1.956(9)	2.06(6)
Co-Bridging CO C (anticlockwise)	1.901(18)	1.939(9)	2.05(7)
C-O Terminal	1.144(5)	1.140(12)	1.022(6^{4})
C-O Bridging	1.178(9)	1.148(11)	1.157(2^{3})
Apical Co - Benzenoid C	2.161(10)	2.122(12)	
Benzenoid C-C	1.411(12)	1.390(18)	

a Estimated standard deviations for the means are given in parentheses (right justified).

b Based on the average lengths. $\sigma_{\bar{l}} = ((\Sigma(l_m - \bar{l})^2)/(m(m-1)))^{\frac{1}{2}}$ where m is the number of observations and $\bar{l}$ is the average length.

Values for $Co_4(CO)_{12}$[22] are included where applicable. It can readily be appreciated that one $Co_4(CO)_9$ group can easily act as a confirmation of the other since the geometries are so similar. Comparison of the bond angle tables will further confirm this.

Caution must be exercised in trusting the geometries of disordered structures and since both the (xylene)$Co_4(CO)_9$ and $Co_4(CO)_{12}$ structures are disordered, one must be doubly cautious. The estimated standard deviations of the disordered structures must be viewed with an appreciable degree of skepticism and one should assure that the difference exceeds 3σ before any definitive arguments are made. However independent confirming trends can often add appreciable weight to statistically weak arguments.

Similar trends are observed for the (xylene)- and (benzene)$Co_4(CO)_9$ complexes. The lengths of bridged (2.457(2)Å) and non-bridged (2.485(1)Å) Co-Co bonds differ significantly. The difference between terminal and bridging carbonyl carbon-oxygen bonds is smaller for the benzene complex than for the xylene complex. Differences between average Co-C (bridging carbonyl) bond lengths are also smaller in the benzene complex to the point of being almost fortuitous.

The bridging carbonyl C-O bond length is 0.03Å shorter in the benzene complex than in the xylene complex. In point of fact, the terminal and bridging carbonyl C-O distances are equal within estimated standard deviations which is somewhat unusual when one considers the spread of distances observed for bridged and non-bridged metal-metal bonds (terminal C≡O: 1.12 - 1.19Å, edge bridging C-O: 1.165 - 1.20Å).[24]

The angle between the plane Co1-Co2-CB1 and the plane Co1-Co2-Co3 is 11.4(3)°, a value lower than that for the xylene complex. This difference is rather puzzling since one would expect the bulkier xylene groups to increase this angle with respect to a benzene ligand. The contrary effect is observed.

The average cobalt-arene carbon distance is 2.122Å for (benzene)$Co_4(CO)_9$. The distance of Co4 to the least squares plane of the benzene ring is 1.603(2)Å. The average benzene carbon-carbon distance is 1.390(5)Å, shorter than that reported for (xylene)$Co_4(CO)_9$ and other π arene transition metal complexes. This value is the same as that for free benzene however. Libration corrections were attempted although they were unsuccessful due to computer program difficulties associated with the three-fold symmetry. The solution produced was not reasonable.

This structural study confirms the infrared analysis of Bor *et al.*[388] The angles measured fall within the ranges specified in this paper. The angle α_2 (see Section A, Part 5) is 99.6^{o} for the benzene complex and 99.1^{o} in the xylene complex. It is also observed that α_1 does increase with increasing substitution on the arene (xylene complex: 99.7^{o}, benzene complex: 98.9^{o}) but the difference is minimal.

The thermal parameters in the (benzene)$Co_4(CO)_9$ complex were all well-behaved. No thermal ellipsoid diagrams were prepared but Table V-C-9 gives the major, median and minor axes of the thermal ellipsoids for the individual atoms and their associated direction cosines. Again here the axis lengths are in units of *B* as with the xylene complex. The packing diagram for the rhombohedral cell given in Figure V-C-5 is a projection down the *b* axis. No large intramolecular or intermolecular distances were recorded up to 3.0Å and those that were found are listed in Tables V-C-10 and V-C-11, respectively.

A final comment must be added concerning the nature of the π bonded aromatic ring. The C-C distances in this complex do not vary significantly (1.387(18) and 1.394(18)Å) and have an average value equal to the C-C distances in free benzene. The localized bonding scheme proposed from the alternating bond lengths in the benzene moiety of benzenetricarbonylchromium (1.401(1) and 1.419(1)Å)[262]

TABLE V-C-9

THERMAL VIBRATION ELLIPSOIDS[a] - BENZENEENNEACARBONYLTETRACOBALT

Atom	Axes[b]	Direction Cosines		
Co1	3.70	0.71930	0.62083	0.31175
	2.94	0.68379	-.55348	-.47549
	2.37	-.12265	0.55519	-.82263
Co4	3.37	0.63592	-.73894	0.22266
	3.36	0.52068	0.19800	-.83048
	2.97	0.56959	0.64405	0.51066
C1	7.79	-.01639	0.57485	-.81810
	5.45	0.30070	-.77749	-.55234
	3.71	0.95358	0.25506	0.16011
C2	7.33	0.11504	0.64381	-.75649
	6.13	0.98878	-.00115	0.14939
	3.30	0.09531	-.76519	-.63671
C11	6.20	0.73717	0.49339	0.46168
	3.73	0.64337	-.30369	-.70274
	2.98	0.20652	-.81507	0.54130
O11	10.09	0.86996	-.02935	-.49226
	6.67	-.13093	0.94866	-.28793
	4.23	0.47543	0.31493	0.82145
C12	5.62	0.38714	-.00739	0.92199
	4.34	0.23902	0.96659	-.09261
	2.88	0.89050	-.25623	-.37597
O12	10.22	0.45486	0.32042	0.83092
	6.89	0.88450	-.27126	-.37958
	2.63	0.10377	0.90760	-.40680
CB1	6.12	0.78077	0.45138	0.43204
	3.75	0.56201	-.80950	-.16991
	2.92	0.27305	0.37547	-.88570
OB1	12.26	0.73086	0.58600	0.34992
	4.59	0.17759	0.33176	-.92650
	2.34	0.65902	-.73928	-.13840

a Given in the order of major, median and minor axes.

b Axis lengths are in units of B where the root mean square displacement $(\bar{U}^2)^{\frac{1}{2}} = (B/8\pi^2)^{\frac{1}{2}}$

Figure V-C-5. A projection down the *b* axis of the rhombohedral cell showing the two molecules of benzeneenneacarbonyltetracobalt(0).

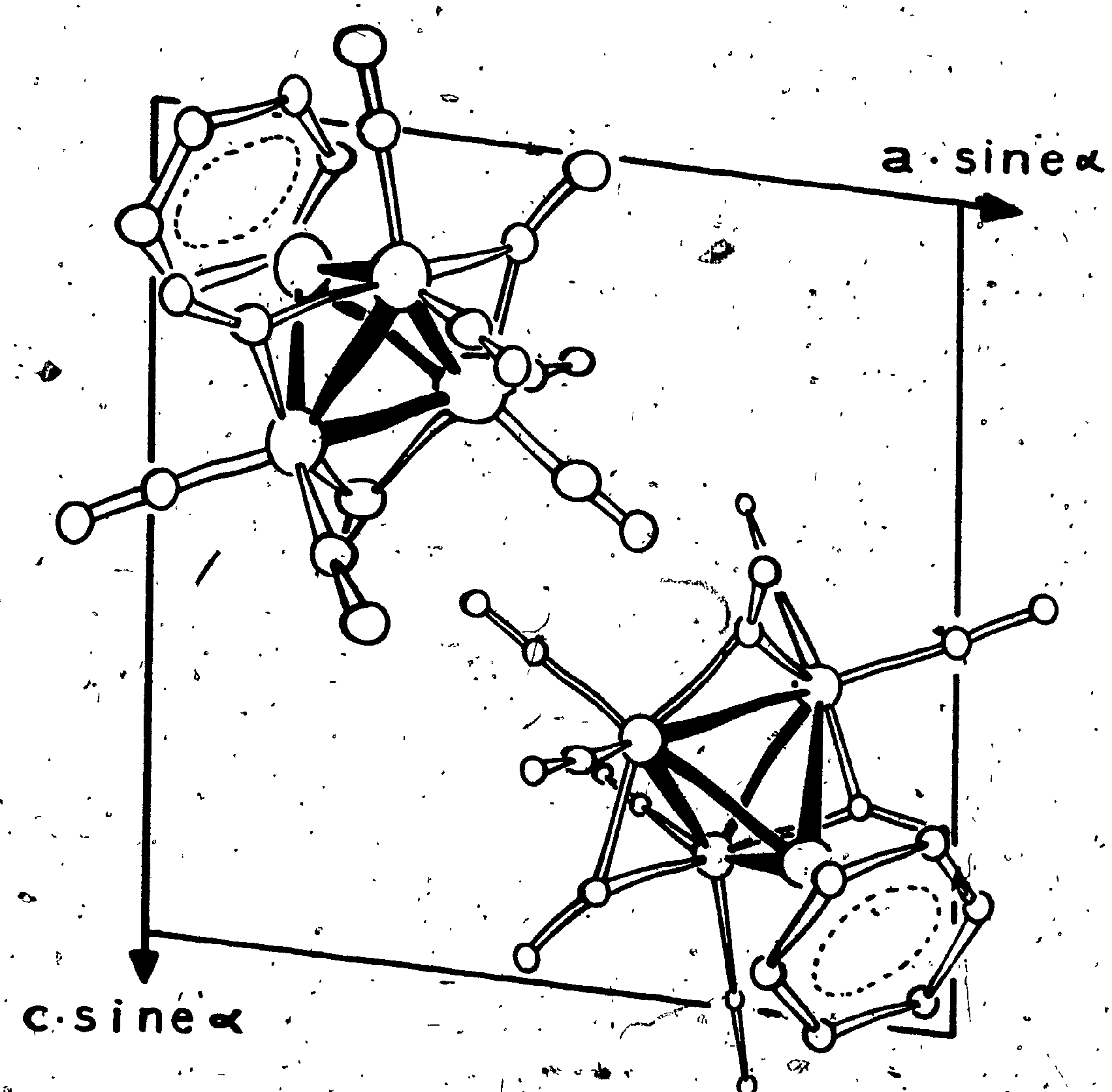

a·sineα
c·sineα

TABLE V-C-10

NON-BONDED INTRAMOLECULAR CONTACTS (Å) FOR (BENZENE)$Co_4(CO)_9$ [a]

Co4-CB1:	2.788	C11-C12:	2.724
CB1-C11:	2.914	CB1-C12:	2.763
CB1-C21:	2.852	CB1-C22:	2.741

[a] Only atomic contacts less than 3.0Å are quoted. Intra-ring distances are not listed.

TABLE V-C-11

INTERMOLECULAR CONTACTS (Å) FOR BENZENEENNEACARBONYLTETRACOBALT[a]

OB3-H2	2.714	O12-H1	2.970

[a] Only atomic contacts less than 3.0Å are quoted. The following transformations give the position of the second atom listed relative to the first which has co-ordinates x,y,z, listed in Table E-2, Appendix E.

$1 - x, -y, -z$

is not found in benzeneenneacarbonyltetracobalt. Perhaps a low temperature study would give different results in this regard.

Gilson[397] has observed a low barrier to rotation (<2.7 kcal $mole^{-1}$) of the benzene ring in benzeneenneacarbonyltetracobalt. This conclusion was reached from nmr data recorded in the solid state. If the arene is rotating, the anisotropic parameters do not indicate that the libration of the ring is considerably greater than vibration of the individual atoms. Thus, the atoms must be spending most time in specific crystallographic sites rather than in free motion. It is interesting to speculate whether the rotation is not responsible for time-averaging the carbon atom positions. A low temperature X-ray crystallographic structure investigation might settle this question.

APPENDIX A

TABLE A-1: The observed and calculated structure factors for tris(hexacarbonyldicobalt-π-ethynyl)arsine.

TABLE A-2: Final positional parameters with estimated standard deviations for tris(hexacarbonyldicobalt-π-ethynyl)-arsine.

TABLE A-3: Final thermal parameters ($x10^4$) with estimated standard deviations for tris(hexacarbonyldicobalt-π-ethynyl)arsine.

TABLE A-1

K	L	FOBS	FCAL
H = -12			
0	6	376	268
0	10	382	265
1	4	434	406
2	6	299	213
2	10	432	395
3	4	277	330
3	10	455	565
4	4	539	497
4	5	357	311
4	8	358	303
5	6	381	325
H = -11			
0	8	363	425
0	10	296	366
0	12	315	191
0	14	629	710
1	0	410	412
1	1	395	505
1	2	378	437
1	4	279	196
1	5	304	230
1	6	319	192
1	7	694	758
1	8	464	569
1	9	340	347
1	10	558	532
1	13	537	604
2	2	315	393
2	3	388	365
2	4	320	363
2	9	387	426
2	11	394	470
2	12	290	297
2	13	440	394
3	0	265	202
3	2	261	297
3	4	715	786
3	6	753	803
3	8	490	515
3	9	304	262
3	11	275	159
3	12	526	484
4	3	290	258
4	5	439	497
4	10	325	419
4	11	471	612
4	13	392	412
5	5	614	630
5	7	498	526
5	8	307	345
5	10	466	568
5	12	316	315
6	3	329	359
6	6	423	392
6	7	288	288
6	8	411	398
6	10	306	280
7	2	578	599
7	3	401	380
7	6	593	636
7	8	712	771
7	9	381	322
7	10	340	310
8	3	355	191
8	4	306	239
8	10	277	196
9	4	449	417
9	6	708	678
9	7	319	381
9	8	450	439
H = -10			
0	0	270	173
0	2	252	326
0	4	581	591
0	8	402	328
1	0	555	543
1	1	592	624
1	2	527	568
1	5	852	916
1	6	471	470
1	7	687	784
1	8	303	268
1	13	346	340
2	1	427	461
2	2	291	303
2	3	501	487
2	4	366	438
2	8	359	446
2	10	688	680
2	12	411	421
2	15	405	428
3	0	734	762
3	2	474	425
3	3	284	358
3	6	603	874
3	7	410	282
3	8	1345	1492
3	9	389	430
3	10	1033	1132
3	14	644	711
3	15	300	169
4	0	332	382
4	1	612	665
4	2	752	[illegible]
4	3	771	[illegible]
4	4	616	[illegible]
4	5	334	292
4	7	291	352
4	8	524	516
4	10	530	532
4	15	394	413
5	1	460	384
5	2	434	516
5	4	449	464
5	5	502	546
5	7	533	583
5	8	300	378
5	9	453	501
5	10	258	187
5	13	535	552
6	9	476	518
6	11	398	289
7	0	700	717
7	1	355	254
7	2	348	393
7	4	280	304
7	5	342	408
7	6	462	551
7	7	404	391
7	8	290	258
7	11	284	372
7	13	333	233
8	4	295	270
8	6	327	297
8	9	287	200
8	12	349	234
8	13	391	376
9	0	701	643
9	1	597	622
9	2	488	428
9	3	431	452
9	6	622	727
9	7	625	736
9	8	691	696
9	10	423	455
10	0	393	378
10	2	720	788
10	3	561	584
10	4	396	425
10	5	623	587
10	6	324	285
10	8	349	351
10	11	307	321
11	6	405	422
11	7	692	756
11	9	639	778
12	7	383	396
H = -9			
0	0	856	841
0	2	761	819
0	4	729	743
0	6	267	329
0	8	1005	1079
0	10	654	656
0	12	282	286
0	14	282	263
1	0	495	394
1	2	349	299
1	3	297	332
1	4	609	641
1	5	391	406
1	6	350	342
1	7	296	338
1	8	343	315
1	9	643	641
1	10	417	369
1	11	430	479
1	15	333	396
2	0	261	134
2	1	608	648
2	2	590	659
2	4	320	408
2	8	305	277
2	9	424	376
2	11	370	425
2	16	459	480
3	0	927	902
3	1	377	364
3	2	1423	1503
3	3	398	341
3	4	933	992
3	5	387	227
3	6	304	298
3	8	897	936
3	9	337	377
3	10	668	728
3	11	288	274
3	12	413	464
3	15	314	203
4	0	782	824
4	1	324	307
4	2	695	653
4	5	403	418
4	8	379	356
4	9	420	518
4	10	413	489
4	11	341	367
4	14	398	374
4	15	392	368
4	16	464	434
5	1	610	647
5	4	303	225
5	7	694	713
5	8	327	183
5	9	666	706
5	10	360	277
5	11	477	397
5	15	372	405
6	0	432	430
6	1	716	726
6	2	458	504
6	3	531	530
6	5	268	142
6	6	331	329
6	7	635	670
6	8	598	611
6	9	360	409
6	10	526	[illegible]
7	2	348	313
7	4	334	317
7	7	277	182
7	9	348	262
7	11	278	247
7	13	267	144
8	2	327	407
8	4	691	734
8	6	441	488
9	0	502	472
9	1	374	332
9	2	292	382
9	4	301	266
9	5	290	275
9	8	334	285
9	10	600	657
9	12	547	563
9	14	318	198
10	0	410	421
10	3	297	410
10	5	334	395
10	8	318	230
10	9	417	376
10	11	388	314
11	1	672	689
11	3	549	602
11	7	636	720
11	9	682	805
11	11	386	364
12	0	481	488
12	1	571	634
12	2	480	375
12	3	500	477
12	7	404	451

K	L	FOBS	FCAL
13	3	287	203
13	5	419	366
13	8	329	422
14	4	289	203
14	5	316	250
14	6	437	574

H = -8

K	L	FOBS	FCAL
0	0	1087	1169
0	2	1719	1758
0	4	1015	1013
0	6	415	424
0	8	297	317
0	10	488	416
0	14	543	532
0	16	747	741
1	3	1336	1352
1	4	491	473
1	5	1312	1409
1	6	405	498
1	9	1421	1475
1	10	915	961
1	11	1171	1215
1	12	624	664
1	13	317	353
1	16	358	366
2	0	238	214
2	3	316	227
2	4	512	540
2	5	326	219
2	8	822	862
2	10	902	944
2	11	398	327
2	14	327	302
2	16	424	396
2	17	319	229
3	1	268	294
3	2	489	428
3	3	225	121
3	4	591	629
3	5	498	528
3	6	838	943
3	7	372	469
3	8	925	1051

K	L	FOBS	FCAL
3	11	340	261
3	12	801	826
3	14	779	774
4	1	540	608
4	2	968	1609
4	3	727	807
4	4	612	549
4	7	395	395
4	8	598	617
4	9	272	292
4	10	411	430
4	12	309	207
4	16	276	175
5	1	817	834
5	2	381	407
5	3	873	878
5	4	677	728
5	5	561	626
5	7	359	355
5	9	329	340
5	13	732	731
6	0	414	376
6	1	415	403
6	2	1024	1053
6	4	843	879
6	5	423	404
6	6	397	375
6	9	488	540
6	11	495	519
6	14	396	335
6	15	450	456
6	16	363	495
7	0	282	272
7	1	425	355
7	2	311	352
7	3	528	499
7	4	863	843
7	5	444	451
7	6	315	284
7	8	777	819
7	9	719	770
7	10	935	984
7	11	659	679
7	12	292	368
7	13	282	281

K	L	FOBS	FCAL
7	14	279	201
7	16	384	414
8	0	253	165
8	1	487	628
8	3	484	485
8	6	384	388
8	7	485	478
8	8	482	497
8	11	332	258
8	13	265	179
8	15	311	212
9	1	380	405
9	2	312	250
9	4	590	622
9	5	432	452
9	6	554	536
9	7	574	639
9	11	474	532
9	12	345	418
9	13	367	391
10	0	275	298
10	1	437	406
10	2	346	394
10	3	326	275
10	6	380	201
10	8	410	424
10	12	307	193
10	14	296	284
11	1	514	419
11	3	371	316
11	4	301	386
11	6	343	427
11	10	397	403
11	11	550	491
11	12	417	377
11	13	733	823
12	4	413	456
12	6	654	676
12	8	297	395
12	9	343	346
12	12	486	381
13	0	289	248
13	2	592	507
13	4	499	534
13	8	552	540

K	L	FOBS	FCAL
13	10	608	663
13	11	411	253
14	0	350	413
14	1	491	473
14	3	575	633
15	4	468	470
15	6	284	243
15	7	306	169

H = -7

K	L	FOBS	FCAL
0	0	990	1051
0	2	334	303
0	6	1402	1499
0	8	1663	1746
0	10	1052	1080
0	14	507	519
0	16	412	479
1	0	315	328
1	1	967	953
1	2	1183	1235
1	3	2035	2091
1	4	1144	1175
1	5	1329	1341
1	6	519	494
1	7	508	515
1	8	559	562
1	9	422	451
1	10	1193	1241
1	11	785	796
1	12	685	717
1	13	823	830
1	15	484	504
2	0	284	324
2	1	475	451
2	2	882	931
2	3	503	548
2	5	811	815
2	6	392	466
2	7	465	436
2	8	465	453
2	9	466	603
2	10	304	182
2	14	319	327
2	16	282	192

K	L	FOBS	FCAL
3	0	1001	1074
3	2	721	784
3	3	323	305
3	4	504	520
3	6	1258	1255
3	8	484	593
3	9	447	476
3	10	580	613
3	11	543	520
3	12	793	793
3	14	301	207
3	16	354	265
4	0	1060	1106
4	1	291	271
4	2	246	224
4	3	764	805
4	4	436	413
4	5	886	919
4	6	665	661
4	8	303	278
4	9	515	526
4	10	482	540
4	11	392	403
4	14	284	268
4	15	266	185
4	16	343	196
5	3	1198	1176
5	4	465	505
5	5	1737	1807
5	7	1441	1523
5	8	620	682
5	10	465	459
5	11	1000	1064
5	13	815	860
6	0	517	465
6	1	679	765
6	2	478	503
6	3	398	387
6	4	623	615
6	5	370	354
6	6	885	891
6	7	634	689
6	8	1319	1367
6	10	820	819
6	14	426	470

K	L	FOBS	FCAL
6	16	458	430
7	0	364	387
7	1	977	1041
7	2	1900	1959
7	3	1362	1436
7	4	1826	1856
7	5	928	976
7	6	608	659
7	8	511	457
7	9	271	321
7	10	732	770
7	12	720	660
7	13	412	396
7	14	493	455
7	15	465	499
8	2	381	431
8	4	682	766
8	5	323	343
8	6	382	443
8	7	748	760
8	8	293	401
8	9	864	525
8	10	410	348
8	13	438	437
8	15	424	425
9	1	287	203
9	3	709	717
9	4	291	163
9	5	816	828
9	6	264	254
9	7	272	179
9	9	597	566
9	11	486	500
9	12	346	327
9	14	346	268
9	15	403	361
10	0	457	321
10	4	509	485
10	8	303	288
10	14	345	329
11	4	507	557
11	5	812	877
11	6	732	715
11	7	739	767
11	11	764	768

K	L	FOBS	FCAL
11	13	628	630
12	0	683	696
12	1	321	241
12	4	476	558
12	5	454	557
12	6	624	678
12	7	291	373
12	8	425	372
12	10	279	243
13	0	272	228
13	1	292	337
13	2	626	675
13	3	273	286
13	4	832	898
13	5	316	172
13	6	469	523
13	9	335	210
13	10	463	419
13	12	633	684
14	6	288	212
14	7	[illegible]	545
14	9	581	524
14	10	325	260
15	0	354	213
15	2	310	399
15	3	334	365
15	9	375	372
16	3	294	256

H = -6

K	L	FOBS	FCAL
0	0	2627	2639
0	2	1957	2014
0	6	2024	2081
0	8	929	824
0	14	539	551
0	16	561	544
1	0	227	162
1	1	490	484
1	2	624	574
1	3	381	372
1	4	275	267
1	5	712	682
1	6	695	660
1	7	1611	1673

K	L	FOBS	FCAL
1	8	442	510
1	9	1132	1166
1	10	249	292
1	13	685	599
1	14	736	745
1	15	543	594
1	16	462	453
1	17	305	202
2	0	456	489
2	2	390	345
2	3	816	832
2	4	1051	1054
2	5	1199	1250
2	7	1005	1025
2	8	681	683
2	10	696	753
2	13	326	233
2	14	480	486
3	1	612	615
3	2	990	1013
3	3	319	343
3	4	1092	1064
3	5	381	391
3	7	417	417
3	8	946	1009
3	9	305	282
3	10	872	850
3	15	310	356
4	1	891	959
4	2	983	1030
4	3	1284	1322
4	4	768	741
4	5	882	893
4	6	269	253
4	7	377	325
4	8	524	590
4	9	242	160
4	10	414	429
4	11	279	257
4	15	305	249
5	0	273	324
5	2	892	940
5	3	541	519
5	4	962	967
5	5	1060	1091

K	L	FOBS	FCAL
5	7	868	864
5	8	347	310
5	14	306	212
5	15	392	311
5	16	406	325
5	17	363	338
6	0	1749	1803
6	2	1388	1442
6	3	824	872
6	5	808	858
6	6	384	314
6	8	709	688
6	10	396	383
6	11	433	452
6	13	376	286
6	14	389	405
6	15	349	419
7	0	409	467
7	1	232	182
7	2	537	541
7	3	245	143
7	4	563	631
7	5	244	269
7	6	997	1029
7	7	995	1036
7	8	1150	1206
7	9	1008	1041
7	10	490	527
7	12	546	485
7	13	594	631
7	14	695	701
7	15	469	580
7	16	566	537
7	17	308	298
8	1	1414	1522
8	2	394	374
8	4	421	442
8	5	1248	1326
8	6	403	433
8	7	1122	1164
8	8	263	301
8	11	314	264
9	0	332	369
9	1	706	812
9	3	633	665

K	L	FOBS	FCAL
9	10	400	347
9	12	509	480
9	15	290	243
10	2	1010	1081
10	3	482	549
10	4	1236	1264
10	10	289	197
10	12	276	245
11	1	252	188
11	3	912	979
11	5	997	1019
11	8	353	362
11	9	409	410
11	10	282	245
12	0	434	387
12	1	400	345
12	2	283	267
12	3	599	576
12	4	330	418
12	5	531	508
12	8	426	376
12	9	288	330
12	10	734	816
12	11	288	223
12	12	508	484
13	0	318	252
13	4	596	629
13	5	365	400
13	6	895	970
13	7	337	264
13	8	645	668
13	12	454	367
14	0	376	259
14	1	849	864
14	2	319	223
14	3	422	460
14	4	506	641
14	5	355	393
14	6	392	467
14	7	618	709
14	10	327	355
15	0	270	318
15	7	289	194
15	4	328	394
16	6	547	604

K	L	FOBS	FCAL
16	8	300	378

H = -5

K	L	FOBS	FCAL
0	0	1389	1337
0	4	1231	1271
0	6	1471	1565
0	8	2023	2059
0	10	788	842
0	12	754	748
0	14	951	980
0	16	519	429
1	0	673	654
1	1	1570	1551
1	2	1541	1563
1	3	1554	1601
1	4	398	460
1	5	326	256
1	6	429	414
1	7	1682	1734
1	8	1583	1604
1	9	1245	1264
1	10	753	764
1	11	456	467
1	14	600	582
1	15	298	260
1	16	317	257
1	17	311	268
1	18	312	258
2	1	645	673
2	2	716	751
2	3	427	412
2	4	466	473
2	5	521	495
2	6	239	248
2	7	897	887
2	9	489	480
2	11	478	484
2	13	422	416
2	14	339	260
3	0	1598	1660
3	2	1455	1475
3	4	678	630
3	5	325	323
3	7	464	422

K	L	FOBS	FCAL
3	8	580	554
3	9	370	357
3	10	982	986
3	11	549	572
3	13	341	281
3	14	982	974
3	15	328	375
3	16	981	948
3	18	358	307
4	1	427	454
4	2	226	177
4	3	842	842
4	5	272	222
4	6	580	614
4	7	1506	1570
4	8	689	622
4	9	1570	1602
4	10	619	664
4	11	642	655
4	16	286	147
5	0	256	216
5	1	221	243
5	3	437	457
5	5	579	567
5	6	612	628
5	7	407	356
5	8	364	447
5	9	931	947
5	10	824	870
5	11	636	660
5	14	343	235
5	15	537	500
5	17	538	563
6	0	560	549
6	1	494	532
6	2	362	371
6	3	521	520
6	4	391	464
6	6	253	228
6	8	644	664
6	10	314	330
6	11	268	211
6	12	344	365
6	14	712	706
6	16	470	422

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
7	0	870	901	10	14	333	325	16	8	345	368	2	13	668	729	5	13	317	402	9	10	862	857
7	1	1548	1632	10	15	318	208	17	3	477	455	2	14	255	221	5	15	478	476	9	11	476	465
7	2	1479	1494	11	1	859	892	17	6	338	239	3	0	749	777	5	17	384	342	9	12	357	329
7	3	927	955	11	2	551	611	18	4	326	350	3	1	1828	1855	6	0	638	643	9	14	407	353
7	4	750	785	11	3	426	399	18	7	310	186	3	2	1134	1143	6	1	333	359	9	16	561	535
7	6	1047	1076	11	4	663	696					3	3	399	362	6	2	537	587	10	0	1366	1436
7	7	748	776	11	5	473	548	H =	-4			3	4	721	742	6	3	937	940	10	1	1470	1495
7	8	1382	1477	11	7	327	308					3	5	606	561	6	5	269	341	10	2	1705	1735
7	9	588	573	11	8	301	331	0	0	2058	2119	3	6	1816	1856	6	6	881	863	10	3	1185	1217
7	10	805	835	11	9	686	664	0	2	192	137	3	7	389	386	6	7	362	268	10	4	949	929
7	16	394	384	11	10	348	259	0	4	1756	1714	3	8	3151	3233	6	9	722	744	10	5	525	536
8	0	457	471	11	11	607	619	0	6	1040	1091	3	9	430	443	6	10	321	306	10	7	284	226
8	1	738	756	11	15	523	497	0	8	412	364	3	10	2160	2229	6	11	345	344	10	8	587	612
8	3	363	434	12	2	652	701	0	10	695	727	3	11	406	424	6	13	354	301	10	9	395	413
8	4	315	336	12	4	842	900	0	12	300	233	3	14	915	877	7	0	737	732	10	10	573	526
8	5	538	558	12	6	524	585	0	14	314	304	3	16	790	720	7	1	437	430	10	11	340	282
8	6	510	540	12	7	322	282	0	16	347	301	3	18	372	338	7	2	1055	1076	10	12	575	592
8	8	359	332	13	0	494	596	1	0	908	937	4	0	1328	1397	7	4	530	547	10	13	265	246
8	9	471	475	13	1	404	441	1	1	1431	1456	4	1	2205	2195	7	6	249	195	10	14	440	368
8	11	418	335	13	2	815	861	1	2	840	879	4	2	2098	2165	7	7	922	961	10	15	432	328
8	13	773	807	13	4	366	339	1	3	358	357	4	3	1649	1691	7	9	341	280	11	1	549	543
8	15	332	390	13	6	468	445	1	4	271	312	4	4	1204	1209	7	10	669	690	11	2	250	294
8	16	305	193	13	7	362	335	1	5	946	968	4	5	675	684	7	11	298	200	11	3	1033	1090
9	2	518	542	13	8	786	731	1	6	1239	1234	4	6	932	986	7	12	655	651	11	7	1157	1120
9	3	617	622	13	9	332	341	1	7	263	218	4	7	645	645	7	13	345	380	11	9	1390	1410
9	4	823	857	13	10	610	671	1	8	922	915	4	8	1036	1025	7	16	391	275	11	13	477	447
9	6	916	947	14	1	453	451	1	9	535	533	4	9	401	362	8	0	271	237	11	15	546	469
9	7	796	840	14	4	313	324	1	11	594	617	4	10	1053	1081	8	2	320	315	12	0	466	426
9	8	277	333	14	7	523	511	1	12	392	431	4	11	441	365	8	3	557	512	12	1	683	715
9	9	1225	1298	14	9	290	224	1	14	457	468	4	12	418	424	8	5	1611	1638	12	2	549	533
9	11	319	388	14	13	545	476	1	15	258	222	4	13	581	580	8	6	484	498	12	3	645	598
9	12	417	448	15	0	313	366	1	17	330	421	4	14	313	322	8	7	646	694	12	7	609	664
9	13	406	338	15	1	427	479	1	18	330	[illegible]	4	15	502	512	8	9	611	659	12	8	348	242
9	14	432	403	15	2	278	289	2	0	679	659	4	17	267	184	8	11	927	1006	12	9	452	450
9	15	581	579	15	3	272	288	2	1	1449	1413	5	0	286	278	8	13	427	457	12	10	440	446
9	16	365	360	15	4	419	440	2	2	1525	1543	5	1	985	940	9	0	1057	1074	13	0	459	351
10	0	246	352	15	5	306	316	2	3	2743	2651	5	2	882	883	9	1	558	579	13	2	731	729
10	1	466	347	15	6	704	784	2	4	381	358	5	3	1468	1505	9	2	930	1001	13	4	[illegible]	689
10	2	372	400	15	7	622	648	2	5	564	539	5	4	195	142	9	3	795	787	13	6	505	568
10	3	483	426	15	8	305	209	2	6	314	318	5	5	521	497	9	4	457	494	13	8	298	282
10	6	795	859	15	9	344	402	2	7	432	419	5	7	1370	1395	9	5	417	380	13	9	290	292
10	7	598	593	15	10	360	318	2	8	914	909	5	9	1292	1318	9	6	1336	1354	13	10	587	574
10	8	1002	1077	16	0	684	726	2	9	600	614	5	10	334	337	9	7	822	794	13	12	282	272
10	9	759	797	16	2	279	173	2	10	546	532	5	14	463	516	9	8	1114	1142	14	1	297	369
10	10	275	388	16	6	472	567	2	11	898	957	5	12	256	146	9	9	864	920	14	2	309	365

K	L	FOBS	FCAL
14	4	489	498
14	5	851	853
14	7	504	538
14	8	386	396
14	11	378	332
15	0	464	490
15	1	648	676
15	2	328	296
15	3	351	359
15	4	564	605
15	6	376	353
15	7	556	444
15	9	546	519
15	11	471	451
16	0	337	398
16	2	566	677
16	3	375	314
16	4	576	695
16	6	408	315
16	10	489	542
17	7	525	564
17	8	308	301
17	9	481	524
18	1	496	594
18	3	284	290
18	7	409	333
19	2	311	347
19	4	408	477

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K	L	FOBS	FCAL
0	2	3192	3112
0	4	2472	2385
0	6	1354	1423
0	8	2603	2635
0	10	1489	1530
0	12	637	704
0	14	735	729
1	0	268	252
1	1	1097	1072
1	2	697	663
1	3	550	575
1	5	832	845
1	6	583	527
1	8	467	447

K	L	FOBS	FCAL
1	9	730	737
1	10	618	608
1	11	601	632
1	12	503	500
1	14	438	445
1	15	379	369
1	17	286	300
2	0	1836	1768
2	1	1155	1120
2	2	2530	2889
2	3	2260	2172
2	4	1036	994
2	6	1460	1447
2	7	448	485
2	9	349	292
2	11	634	643
2	12	255	238
2	14	509	492
2	16	327	246
3	0	3572	3581
3	1	3005	2928
3	2	2774	2726
3	3	694	621
3	4	899	883
3	5	215	175
3	6	1422	1466
3	8	1163	1170
3	9	214	148
3	10	911	935
3	12	898	893
3	13	517	503
3	14	722	770
4	0	204	169
4	2	1376	1398
4	4	651	690
4	5	1675	1645
4	6	641	683
4	7	1481	1477
4	8	481	522
4	9	446	485
4	10	303	276
4	11	377	400
4	12	833	659
4	13	793	787
4	14	483	498

K	L	FOBS	FCAL
4	15	275	253
4	16	258	130
5	1	1882	1843
5	2	857	867
5	4	553	528
5	5	881	914
5	7	855	874
5	9	523	537
5	10	496	512
5	13	256	210
5	14	280	222
6	0	590	663
6	1	735	757
6	2	2085	2105
6	3	1032	1059
6	4	327	348
6	5	274	322
6	6	808	860
6	7	819	835
6	8	1710	1784
6	9	734	763
6	10	880	879
7	0	686	740
7	1	1065	1151
7	2	730	774
7	3	311	307
7	4	668	691
7	5	886	935
7	6	1053	1078
7	7	642	635
7	9	260	322
7	11	356	342
7	15	310	344
7	16	304	182
7	17	343	188
8	1	1528	1555
8	2	264	218
8	3	2347	2375
8	5	1279	1263
8	7	840	843
8	9	949	969
8	14	261	194
9	0	840	827
9	1	703	735
9	2	1694	1753

K	L	FOBS	FCAL
9	4	820	793
9	5	246	205
9	7	374	305
9	8	754	847
9	10	1091	1110
9	11	387	284
9	12	694	682
9	13	436	454
10	0	460	411
10	1	256	159
10	2	826	855
10	3	237	204
10	4	1478	1501
10	5	797	805
10	6	1126	1142
10	7	900	931
10	8	254	302
10	9	900	910
10	10	391	424
10	12	541	509
10	13	417	394
10	14	295	270
10	15	519	486
11	1	1968	2031
11	3	676	656
11	5	922	977
11	7	1071	1124
11	9	354	364
11	10	351	225
11	13	291	243
11	15	319	184
12	0	857	887
12	3	903	937
12	4	281	178
12	7	692	755
12	8	341	347
12	9	467	576
12	11	335	336
13	3	527	571
13	7	350	265
13	9	278	244
13	10	309	179
14	0	301	294
14	1	463	503
14	2	523	590

K	L	FOBS	FCAL
14	3	1228	1193
14	5	492	492
14	6	356	347
14	7	400	356
14	8	281	284
14	9	399	427
14	13	307	245
15	4	540	616
15	5	311	321
15	8	528	395
15	9	308	302
15	10	684	679
15	11	597	574
15	12	404	400
16	2	616	669
16	4	877	944
16	5	318	294
16	6	620	607
16	7	477	349
17	1	709	738
17	3	507	535
17	7	399	358
17	9	409	424
18	2	407	348
18	4	304	168
18	5	288	236
18	6	413	353
18	8	529	511
19	5	328	268
19	6	324	223

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K	L	FOBS	FCAL
0	0	4808	4674
0	2	4442	4301
0	4	832	814
0	6	1823	1849
0	8	421	427
0	10	308	280
0	12	418	370
0	14	874	974
1	0	441	383
1	1	389	361
1	2	501	429
1	3	431	348

K	L	FOBS	FCAL
1	4	714	716
1	5	1050	1020
1	6	578	562
1	7	409	386
1	9	526	525
1	11	374	336
1	15	291	240
2	0	519	498
2	3	481	396
2	4	190	147
[illegible]	5	1712	1693
2	7	391	374
2	8	723	721
2	9	500	529
2	10	562	541
2	11	363	393
2	12	228	123
2	13	287	171
2	14	462	435
2	17	317	259
3	0	687	659
3	1	602	548
3	2	1059	1038
3	3	635	610
3	4	813	806
3	5	1681	1650
3	6	2386	2404
3	8	2264	2299
3	11	313	343
3	12	1549	1575
3	14	1252	1264
3	16	325	252
4	0	1395	1407
4	1	2799	2720
4	2	392	354
4	4	605	646
4	5	1310	1353
4	6	1325	1318
4	7	869	918
4	8	635	648
4	11	269	202
4	13	323	249
4	15	297	190
5	0	262	273
5	1	682	608

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
5	2	240	197	9	6	857	951	14	3	697	730	1	13	980	1037	5	15	341	341	10	0	1121	1106
5	3	502	567	9	7	895	937	15	2	1078	1170	1	14	395	372	6	0	2616	2604	10	1	215	219
5	7	664	661	9	10	230	191	15	4	1066	1100	1	15	637	564	6	1	2174	2154	10	2	642	643
5	9	356	361	9	12	358	448	15	7	356	338	2	0	1105	1103	6	2	782	721	10	7	436	415
5	10	219	249	9	13	357	354	15	8	374	319	2	1	1833	1721	6	3	426	375	10	12	329	257
5	11	549	554	9	14	634	585	16	1	351	399	2	2	554	549	6	4	1099	1139	10	13	491	434
5	13	1178	1219	9	16	394	373	16	3	325	357	2	3	699	741	6	5	938	920	11	0	486	559
5	15	412	379	10	0	1255	1260	16	6	333	249	2	4	571	548	6	6	2234	2329	11	1	925	903
6	0	1297	1383	10	1	1237	1253	16	8	430	371	2	5	1769	1771	6	7	836	839	11	5	1450	1484
6	1	911	907	10	2	536	537	16	9	493	490	2	7	351	415	6	8	2095	2197	11	6	378	401
6	2	2859	2855	10	3	554	600	16	10	301	384	2	8	351	406	6	10	697	779	11	7	1028	1107
6	3	547	540	10	4	655	670	17	1	303	306	2	9	758	745	6	13	269	281	11	8	336	371
6	4	738	699	10	5	893	879	17	5	312	203	2	11	430	389	6	14	597	546	11	11	512	472
6	8	387	414	10	6	775	856	17	7	406	216	2	13	400	505	6	16	409	336	11	12	304	213
6	10	338	250	10	7	870	1014	17	8	339	332	2	17	339	320	7	1	2321	2411	11	13	457	353
6	11	249	232	10	8	348	254	18	0	437	399	3	0	5123	5136	7	2	347	367	12	0	497	514
6	12	497	516	10	9	445	481	18	2	291	284	3	1	1160	1126	7	3	611	608	12	2	579	694
6	13	374	377	11	2	451	506	18	3	370	339	3	2	2904	2787	7	4	585	595	12	4	579	589
6	14	479	440	11	3	409	415	18	5	546	535	3	4	2279	2256	7	5	258	226	12	5	724	739
6	16	478	421	11	5	466	447	18	6	560	500	3	5	1649	1689	7	6	312	257	12	6	380	377
7	0	452	473	11	6	590	569	18	7	408	327	3	6	2485	2575	7	8	309	255	12	7	698	701
7	1	255	299	11	7	1316	1317	19	0	390	385	3	7	502	458	7	9	445	357	12	9	314	261
7	2	223	163	11	9	429	442	19	1	324	261	3	8	1306	1361	7	11	304	286	12	10	359	393
7	3	251	195	11	11	789	742	19	4	288	279	3	10	333	263	7	12	638	649	12	14	321	205
7	7	721	707	11	13	871	828	19	5	323	265	3	12	275	307	7	13	611	572	13	2	609	559
7	8	510	507	11	15	388	374	20	3	356	306	4	0	1295	1327	7	14	791	736	13	3	993	1012
7	9	1181	1213	12	1	376	362					4	1	408	377	7	15	580	496	13	4	484	493
7	11	330	364	12	2	459	405	H =	-1			4	5	1787	1798	8	1	1378	1401	13	6	704	684
7	12	238	126	12	3	649	669					4	6	721	710	8	2	265	313	13	7	431	404
8	1	1809	1833	12	4	1321	1332	0	2	2463	2309	4	10	626	647	8	3	1266	1271	13	8	291	240
8	2	320	356	12	5	464	546	0	4	1180	1251	4	11	434	497	8	5	1055	1065	13	9	437	350
8	3	312	351	12	6	957	1005	0	6	3831	4051	4	12	499	449	8	6	493	512	13	10	270	308
8	5	819	831	12	10	531	413	0	8	2706	2845	4	13	752	751	8	7	1625	1674	13	11	348	228
8	6	630	675	12	11	371	295	0	12	1298	1389	5	0	363	397	8	9	1265	1314	13	12	603	549
8	7	422	431	12	13	286	240	0	14	1144	1217	5	1	1371	1330	8	11	315	201	14	2	371	427
8	8	407	348	13	2	362	378	0	16	304	338	5	2	1019	975	8	13	390	476	14	3	476	466
8	9	478	495	13	4	268	145	1	2	435	398	5	3	962	946	8	15	275	293	14	5	646	623
8	11	409	418	13	5	299	307	1	3	538	544	5	4	523	454	9	1	900	861	14	6	381	382
8	14	290	172	13	7	487	495	1	4	496	491	5	5	1717	1766	9	2	593	543	14	7	1025	1081
8	15	456	438	13	9	419	437	1	5	1415	1403	5	6	404	363	9	6	626	688	14	9	452	516
9	1	946	1029	13	10	433	323	1	7	950	1002	5	7	1344	1339	9	7	444	418	15	0	371	411
9	2	524	517	13	11	296	171	1	8	332	316	5	8	266	228	9	8	694	781	15	2	343	300
9	3	462	454	13	12	331	290	1	9	465	499	5	10	240	260	9	10	436	451	15	4	305	197
9	4	1182	1173	13	13	314	227	1	11	598	611	5	11	882	916	9	12	253	200	15	9	329	309
9	5	1214	1237	14	1	727	953	1	12	365	353	5	13	745	746	9	14	396	339	15	10	328	371

K	L	FOBS	FCAL
16	0	325	295
16	2	366	483
16	3	273	329
16	5	321	418
16	6	311	282
16	8	349	421
17	6	371	282
17	7	338	312
18	2	328	400
18	4	352	377
19	4	590	594
19	6	349	368

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K	L	FOBS	FCAL
0	2	4356	4734
0	4	1720	1941
0	6	2893	3075
0	8	822	873
0	14	392	370
1	3	764	819
1	4	699	724
1	5	1552	1661
1	6	955	1008
1	7	1616	1724
1	8	583	593
1	9	217	226
1	11	459	409
1	12	587	542
1	13	698	722
1	14	427	411
1	15	309	307
2	1	2000	1952
2	2	366	351
2	3	453	474
2	5	448	483
2	7	1310	1371
2	9	342	362
2	10	298	188
2	11	316	269
2	13	503	426
3	1	481	549
3	2	866	851
3	4	638	693
3	5	357	334

K	L	FOBS	FCAL
3	6	1171	1199
3	7	337	337
3	8	953	967
3	12	823	786
3	14	286	196
3	16	361	236
4	0	677	666
4	1	707	641
4	3	475	519
4	4	1226	1246
4	5	318	279
4	7	231	256
4	8	757	762
4	9	1151	1235
4	10	450	444
4	11	243	275
4	12	303	276
4	13	328	224
4	14	340	281
4	15	252	249
5	1	913	954
5	2	234	244
5	3	1013	1041
5	4	380	425
5	5	681	705
5	7	313	305
5	11	295	242
5	14	284	181
5	15	370	340
6	0	1398	1442
6	1	3257	3146
6	2	2844	2839
6	3	288	230
6	4	393	443
6	5	1006	1013
6	6	1659	1750
6	7	572	631
6	8	1601	1699
6	10	752	792
6	12	488	444
7	1	836	827
7	4	850	866
7	5	1158	1205
7	6	1366	1417
7	7	1362	1421

K	L	FOBS	FCAL
7	8	1180	1229
7	9	866	924
7	11	433	447
7	12	616	536
7	13	726	723
7	14	459	410
7	15	273	301
8	1	2163	2153
8	3	458	494
8	5	1619	1693
8	6	605	566
8	7	1370	1433
8	9	563	566
8	12	443	391
9	1	254	179
9	2	217	256
9	3	386	322
9	4	343	348
10	0	386	369
10	1	845	880
10	2	398	418
10	5	613	611
10	6	413	360
10	7	273	277
10	8	613	657
10	14	334	314
11	1	810	839
11	3	1073	1110
11	4	306	362
11	7	542	543
11	11	359	278
12	0	524	508
12	1	1127	1234
12	2	811	778
12	3	625	671
12	4	1203	1233
12	5	272	294
12	7	527	480
12	8	851	902
12	9	414	411
12	10	791	842
12	12	484	385
13	2	445	430
13	3	604	703
13	4	760	714

K	L	FOBS	FCAL
13	5	550	612
13	6	810	832
13	7	562	559
13	8	487	386
13	12	422	240
13	13	339	342
14	0	294	202
14	1	1760	1773
14	3	411	351
14	5	707	750
14	6	311	365
14	7	593	648
14	8	303	392
15	2	562	635
15	4	417	287
15	6	369	327
16	0	389	470
16	1	467	473
16	3	296	276
16	6	418	484
16	7	355	349
16	9	308	278
18	0	432	332
18	3	361	306
18	4	303	319
18	6	367	276
19	2	567	601
19	3	418	412
19	4	549	578
20	0	406	327
20	1	365	371

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K	L	FOBS	FCAL
0	2	332	343
0	4	2735	2812
0	6	1916	1962
0	8	1238	1258
0	10	398	398
0	12	1321	1318
0	14	731	704
1	1	960	925
1	3	455	465
1	5	712	700
1	6	339	356

K	L	FOBS	FCAL
1	7	414	387
1	8	517	505
1	9	492	491
1	11	584	589
1	12	412	443
2	0	1134	1103
2	1	1205	1214
2	2	337	304
2	3	1122	1153
2	4	597	640
2	5	730	707
2	6	177	188
2	7	696	717
2	8	467	478
2	9	827	861
2	10	229	246
2	13	260	232
3	0	5360	5136
3	1	577	568
3	2	1552	1556
3	3	225	210
3	4	1274	1314
3	6	1285	1339
3	9	230	276
3	10	623	607
3	11	334	282
3	14	398	422
3	16	380	324
4	0	1363	1327
4	1	1216	1227
4	2	1342	1372
4	3	1076	1125
4	5	908	954
4	6	913	928
4	7	1370	1419
4	8	941	1009
4	9	450	433
4	11	412	362
4	12	349	295
4	13	240	227
5	0	348	397
5	1	1982	1967
5	2	402	436
5	3	454	468
5	4	1204	1236

K	L	FOBS	FCAL
5	5	186	116
5	6	493	497
5	8	252	284
5	9	749	778
5	11	771	779
5	12	283	197
6	0	2714	2604
6	2	1675	1693
6	4	427	484
6	5	192	165
6	6	1139	1227
6	8	369	312
6	10	478	496
6	12	801	781
6	14	554	463
7	0	740	789
7	1	1301	1343
7	2	488	561
7	4	381	443
7	5	1235	1293
7	6	396	433
7	7	629	662
7	10	397	426
7	12	475	430
7	14	354	212
8	0	312	299
8	4	341	314
8	5	526	536
8	7	551	581
8	8	268	315
8	11	760	766
8	13	478	499
9	0	529	554
9	2	812	850
9	4	877	915
9	5	362	347
9	7	351	374
9	10	264	204
10	0	1045	1106
10	2	853	873
10	5	391	457
10	6	922	975
10	7	696	766
10	8	640	664
10	9	399	444

K	L	FOBS	FCAL
11	0	529	559
11	1	976	1010
11	4	290	272
11	5	798	896
11	6	318	388
11	9	563	590
11	10	299	239
11	11	381	327
12	1	533	514
12	2	1333	1450
12	3	430	476
12	4	1089	1127
12	8	337	317
12	12	278	164
13	0	370	427
13	1	931	967
13	2	375	444
13	3	279	268
13	4	391	350
13	5	323	348
13	7	533	539
13	8	525	471
13	10	486	434
13	12	376	286
14	0	259	248
14	1	244	310
14	3	344	260
14	5	438	445
14	6	324	188
14	7	320	330
14	11	536	544
15	0	456	411
15	4	642	743
15	6	492	510
15	10	461	408
16	0	284	295
16	3	354	241
16	8	312	231
17	0	256	150
17	1	266	280
18	1	541	543
18	2	499	486
18	3	525	475
19	4	368	412
19	2	287	191

K	L	FOBS	FCAL
19	5	351	248
20	0	319	242
20	1	454	395

H = 2

K	L	FOBS	FCAL
0	0	4833	4674
0	2	512	506
0	4	1881	1915
0	6	1915	1947
0	8	420	374
0	10	719	719
0	12	305	351
1	0	440	383
1	1	292	243
1	2	189	162
1	3	1100	1146
1	4	1143	1111
1	5	1458	1466
1	6	612	645
1	7	606	612
1	9	439	375
1	10	593	608
1	11	976	1040
1	12	754	765
1	13	394	358
2	0	531	498
2	1	661	657
2	2	824	772
2	3	2210	2221
2	4	1053	1082
2	5	1589	1639
2	6	321	317
2	7	610	636
2	8	275	269
2	9	572	531
2	10	286	290
2	11	714	696
2	13	525	491
2	15	299	289
3	0	697	659
3	1	200	179
3	2	742	745
3	3	849	854
3	4	915	921

K	L	FOBS	FCAL
3	6	1567	1589
3	7	371	344
3	8	1481	1569
3	9	301	303
3	10	442	454
3	11	359	385
3	12	262	246
3	14	355	325
4	0	1420	1407
4	1	2397	2313
4	2	1047	1041
4	3	606	592
4	4	710	734
4	5	321	277
4	6	411	404
4	7	357	347
4	9	226	143
4	10	401	294
4	11	481	447
4	12	524	524
4	13	633	599
4	14	464	404
4	15	291	240
5	0	294	273
5	1	1435	1415
5	2	601	628
5	3	828	894
5	4	610	657
5	6	401	357
5	7	394	370
5	8	278	204
5	9	702	715
5	11	401	317
6	0	1325	1383
6	1	291	327
6	4	2229	2300
6	5	663	659
6	6	1698	1765
6	7	254	328
6	8	390	473
6	11	388	322
6	12	384	332
7	0	471	473
7	1	264	202
7	3	505	590

K	L	FOBS	FCAL
7	4	1463	1552
7	5	908	965
7	6	1093	1170
7	7	648	756
7	9	351	276
7	10	775	736
7	11	701	681
7	12	681	690
7	13	406	387
7	14	284	176
8	1	474	490
8	3	1996	2115
8	4	237	153
8	5	1942	2011
8	6	211	128
8	7	362	338
8	9	542	584
8	11	516	528
8	13	302	231
9	1	534	598
9	2	610	624
9	3	598	623
9	4	367	328
9	5	366	366
9	6	453	536
9	8	582	635
9	9	436	412
9	10	344	362
9	11	302	306
10	0	1266	1280
10	1	792	785
10	2	1183	1214
10	3	507	527
10	4	363	302
10	5	631	646
10	7	297	239
10	10	345	301
10	12	639	599
10	13	372	248
11	0	264	298
11	1	599	592
11	2	335	350
11	3	731	779
11	4	434	456
11	5	432	465

K	L	FOBS	FCAL
11	6	418	421
11	7	978	1047
11	8	243	201
11	9	389	436
12	0	275	265
12	3	411	405
12	5	487	519
12	7	376	355
12	8	536	554
12	10	260	234
13	1	448	527
13	2	503	525
13	3	331	301
13	4	757	800
13	5	267	327
13	6	395	481
13	10	434	382
14	3	727	746
14	4	321	349
14	5	770	850
14	6	378	347
14	7	349	300
14	9	382	250
15	1	490	472
15	2	414	449
15	9	341	337
16	1	345	282
16	2	554	500
16	4	663	741
16	6	280	227
16	7	334	302
17	4	293	318
17	7	374	360
18	0	414	399
19	0	394	385
19	1	445	314
19	2	565	595
19	4	369	354

H = 3

K	L	FOBS	FCAL
0	2	1494	1508
0	4	857	865
0	6	436	[illegible]
0	8	680	[illegible]

K	L	FOBS	FCAL
0	14	260	130
1	0	250	252
1	3	569	623
1	4	423	404
1	5	350	347
1	7	207	161
1	8	303	370
1	9	354	437
1	10	295	295
1	11	277	321
2	0	1826	1788
2	1	363	364
2	2	1503	1471
2	3	1728	1786
2	4	1016	1027
2	5	1802	1909
2	6	455	462
2	7	1043	1094
2	10	238	140
2	11	480	458
2	12	325	341
2	13	344	351
3	0	3647	3561
3	1	872	895
3	2	1204	1210
3	3	180	192
3	4	1020	1058
3	5	279	263
3	6	1151	1150
3	7	323	316
3	8	770	783
3	10	517	508
3	12	588	503
3	14	427	345
4	3	1086	1109
4	4	1833	1870
4	5	2114	2140
4	6	1754	1799
4	7	1493	1586
4	8	834	843
4	10	610	611
4	11	793	757
4	12	673	662
4	13	557	465
4	14	338	252

K	L	FOBS	FCAL
5	1	1151	1142
5	2	219	261
5	3	516	505
5	4	214	256
5	5	411	344
5	7	255	293
5	11	259	222
5	13	355	216
6	0	620	663
6	1	263	247
6	2	381	417
6	3	502	515
6	4	619	626
6	5	480	423
6	7	380	266
6	9	381	320
6	11	320	281
7	0	702	740
7	1	692	644
7	2	266	210
7	3	1158	1157
7	5	971	981
7	8	292	201
7	9	351	365
8	0	283	290
8	1	1209	1234
8	3	1837	1872
8	5	683	694
8	6	325	323
8	10	330	250
9	0	849	827
9	1	329	344
9	2	902	926
9	3	485	274
9	5	252	235
9	6	589	569
9	7	375	349
9	8	795	763
9	9	247	227
9	10	456	513
9	12	297	276
10	0	441	411
10	1	224	179
10	2	551	574
10	3	543	578

K	L	FOBS	FCAL
10	4	1460	1531
10	5	523	926
10	6	1590	1685
10	7	758	755
10	8	252	352
10	10	475	410
10	11	435	299
10	12	529	490
11	1	1177	1207
11	3	260	197
11	5	784	765
11	11	307	178
12	0	877	887
12	1	447	445
12	2	626	664
12	3	785	781
12	5	937	974
12	6	432	449
12	11	362	322
13	0	374	364
13	6	321	225
14	0	308	294
14	1	470	388
14	2	425	470
14	3	526	510
14	4	615	618
14	6	336	234
15	2	517	502
15	4	593	612
15	8	508	507
15	9	447	316
16	1	285	196
16	2	748	821
16	3	344	281
16	4	825	852
16	6	415	442
17	1	521	478
17	5	278	196
18	2	317	311
18	5	439	448

H = 4

K	L	FOBS	FCAL
0	0	1992	2119
0	4	769	783

K	L	FOBS	FCAL
0	8	280	224
0	12	388	332
1	0	908	937
1	1	274	172
1	3	447	501
1	4	634	593
1	5	1197	1240
1	6	860	907
1	7	572	604
1	10	301	221
1	12	242	150
2	0	669	659
2	3	787	786
2	5	745	777
2	6	320	282
2	7	610	650
2	8	223	153
2	9	269	256
2	10	287	204
3	0	710	777
3	1	292	227
3	2	353	362
3	3	364	304
3	4	728	740
3	6	1063	1058
3	8	386	406
3	10	503	464
3	12	713	706
4	0	1342	1397
4	1	937	969
4	2	324	283
4	3	1216	1244
4	4	1145	1132
4	5	1478	1505
4	6	641	656
4	7	794	803
4	11	275	208
4	12	335	256
5	0	306	278
5	2	301	292
5	3	485	527
5	4	317	252
5	5	267	183
5	7	328	272
5	11	294	290

K	L	FOBS	FCAL
6	0	633	643
6	1	430	463
6	2	688	735
6	3	566	543
6	4	359	282
7	0	715	732
7	1	933	914
7	4	913	961
7	5	549	583
7	6	853	923
7	7	580	556
7	10	321	337
7	11	272	273
7	12	259	208
8	0	232	237
8	2	497	471
8	3	382	359
8	4	230	243
8	6	225	113
8	7	795	778
8	8	347	285
8	9	559	543
9	0	1040	1074
9	1	382	399
9	2	1089	1150
9	3	393	421
9	4	575	569
9	5	454	435
9	6	433	333
9	9	282	185
9	10	243	170
10	0	1381	1436
10	1	660	624
10	2	257	237
10	3	454	448
10	4	795	837
10	5	677	698
10	6	695	769
10	7	337	297
10	8	387	340
10	9	260	178
10	10	255	167
11	1	470	521
11	2	370	406
11	4	469	463

K	L	FOBS	FCAL
11	5	596	619
11	6	254	159
11	7	322	380
11	10	279	198
12	0	429	426
12	2	353	386
12	3	395	426
12	4	599	658
12	8	272	205
13	0	358	351
13	2	279	255
13	4	502	474
15	0	542	490
15	1	451	506
15	2	704	728
15	4	466	451
16	0	434	398
16	6	578	519
17	1	440	401
17	2	318	288
17	3	431	409
17	4	341	267
17	5	373	352
18	0	265	160
18	3	338	269

H = 5

K	L	FOBS	FCAL
0	0	1331	1337
0	2	1445	1499
0	4	599	662
0	6	1479	1558
0	8	925	961
0	12	342	246
1	0	638	654
1	2	536	555
1	3	611	659
1	4	341	393
1	5	254	294
1	6	275	203
1	7	269	289
1	8	392	325
1	9	266	232
1	11	349	256
1	12	287	256

K	L	FOBS	FCAL
2	1	917	953
2	2	844	884
2	3	903	847
2	4	352	361
2	5	242	240
2	7	460	478
2	9	621	571
2	10	334	407
2	11	577	499
3	0	1563	1660
3	1	357	401
3	2	192	133
3	3	451	470
3	4	940	1025
3	5	230	158
3	6	790	850
3	7	227	234
3	8	282	298
4	1	354	307
4	2	337	411
4	3	417	467
4	4	870	944
4	5	852	915
4	6	512	556
4	8	358	310
4	9	679	649
4	10	795	711
4	11	561	584
4	12	470	421
5	0	244	216
5	2	493	489
5	3	327	348
5	4	563	562
5	5	300	225
5	8	309	218
6	0	576	549
6	1	527	511
6	3	959	993
6	4	490	452
6	6	728	826
6	8	514	467
6	9	328	223
7	0	838	901
7	1	678	662
7	3	238	323

K	L	FOBS	FCAL
7	4	697	772
7	5	349	320
7	8	371	267
8	0	495	471
8	1	1402	1424
8	2	279	160
8	3	675	659
8	5	381	489
8	7	685	710
8	9	483	425
9	1	369	445
9	3	623	655
9	4	331	209
9	6	640	651
9	7	301	343
9	8	494	457
10	0	337	352
10	1	314	325
10	2	717	720
10	3	484	394
10	4	897	917
10	5	320	278
10	6	393	323
10	8	401	385
10	9	296	231
10	10	567	481
11	2	587	608
11	3	724	720
11	4	516	488
11	5	464	512
11	6	277	140
11	9	278	169
12	1	239	193
12	2	314	441
12	3	359	319
12	4	315	293
12	5	261	273
12	9	399	331
13	0	488	596
13	1	498	448
13	3	299	218
14	1	758	796
14	2	347	374
14	3	265	160
14	4	311	308

K	L	FOBS	FCAL
14	5	467	445
14	7	623	613
15	0	323	386
15	3	271	195
16	0	683	726
16	1	295	189
16	2	602	618
17	3	423	346
H = 6			
0	0	2436	2639
0	2	1362	1431
0	6	670	680
0	8	516	470
0	10	563	524
1	1	281	307
1	2	697	746
1	3	621	659
1	4	926	972
1	5	935	952
1	6	807	819
1	7	572	513
1	11	377	387
2	0	455	489
2	1	1248	1317
2	2	659	689
2	3	931	996
2	5	626	644
2	6	278	192
2	7	318	338
2	9	523	440
2	11	334	308
3	1	364	373
3	2	284	310
3	3	439	470
3	6	314	301
3	8	272	204
3	10	366	313
4	1	591	560
4	2	1183	1246
4	3	1583	1696
4	4	1157	1239
4	5	503	487
4	7	525	490

K	L	FOBS	FCAL
4	8	476	495
4	9	514	493
4	10	309	197
5	1	337	336
5	2	376	415
5	3	639	609
5	4	490	414
5	5	261	241
6	0	1724	1803
6	1	1090	1130
6	2	986	1017
6	3	533	538
6	5	308	192
6	6	334	410
6	7	325	285
6	8	566	586
6	10	473	525
7	0	493	467
7	3	670	701
7	4	972	1000
7	5	753	754
7	6	750	742
7	7	417	404
7	10	446	361
8	1	1028	1093
8	2	331	367
8	3	397	324
8	4	286	275
8	8	290	267
9	0	433	369
9	1	233	211
9	2	381	402
9	3	238	196
9	6	328	313
9	8	246	125
10	2	886	863
10	3	258	231
10	4	557	621
10	5	325	324
10	8	436	464
11	1	753	757
11	3	411	392
11	6	276	148
12	0	382	387
12	1	756	769

K	L	FOBS	FCAL
12	2	527	544
12	3	650	702
12	4	357	327
12	6	307	200
12	7	377	369
13	0	255	252
13	2	476	509
13	3	359	376
13	4	388	442
13	5	391	380
13	6	400	360
14	0	262	259
14	1	589	604
14	2	487	468
14	4	354	266
15	0	351	318
15	3	270	141
15	4	312	236
16	3	323	212
H = 7			
0	0	920	1051
0	2	981	1020
0	4	1271	1323
0	6	660	681
0	8	317	190
0	10	675	572
1	0	310	328
1	1	437	466
1	2	733	760
1	3	1118	1144
1	4	527	547
1	5	469	513
2	0	284	324
2	1	777	819
2	3	523	513
3	0	959	1074
3	1	539	550
3	2	291	227
3	4	299	269
3	5	270	214
4	0	1038	1106
4	1	575	618
4	2	519	512

K	L	FOBS	FCAL
4	4	280	191
4	5	278	405
4	6	316	398
4	7	333	290
5	1	310	333
5	3	352	294
5	5	274	257
5	8	386	242
6	0	455	465
6	1	263	218
6	2	1107	1125
6	4	839	886
6	6	346	315
7	0	359	387
7	2	701	697
7	3	538	558
7	4	556	611
7	5	563	547
8	3	449	495
8	5	621	603
9	1	554	608
9	2	285	370
9	3	292	324
9	4	305	338
10	0	274	321
10	2	421	409
10	6	334	321
11	2	413	371
12	0	645	696
12	1	433	402
12	2	627	659
12	3	264	174
12	4	265	288
13	4	326	354
14	3	434	447
15	0	288	213
H = 8			
0	0	982	1169
0	2	451	417
0	4	948	1039
0	6	328	308
1	0	263	226
1	2	395	384

K	L	FOBS	FCAL
1	4	528	599
1	5	412	415
2	1	314	374
2	4	363	330
2	5	289	220
2	6	304	283
2	7	353	264
3	1	254	150
3	2	456	482
3	4	591	554
3	6	409	400
4	2	400	479
4	3	352	225
4	6	477	416
4	7	348	404
4	8	272	255
5	1	315	304
5	2	252	268
6	0	431	376
6	2	370	438
6	4	580	580
6	5	355	357
6	6	537	573
7	0	338	272
7	4	445	446
7	5	263	214
7	6	397	385
8	2	381	322
8	3	425	464
8	4	309	160
8	5	431	443
9	1	260	215
9	6	316	180
10	1	249	178
11	1	376	241
11	3	266	314
13	0	303	240
13	1	479	480
14	0	437	413
H = 9			
0	0	699	841
0	2	401	385
1	0	396	394

K	L	FOBS	FCAL
1	1	635	679
1	2	589	579
1	3	571	572
1	6	261	218
2	1	438	482
2	2	[illegible]	371
2	4	[illegible]	482
2	5	429	473
2	6	268	295
3	0	768	982

K	L	FOBS	FCAL
4	0	798	424
4	3	365	380
4	4	648	685
4	5	752	729
4	6	437	518
5	1	569	597
5	3	383	276
6	0	408	430
6	2	383	316
6	3	282	252

K	L	FOBS	FCAL
7	1	348	347
7	2	452	477
7	3	579	614
7	4	445	447
9	0	393	472
9	1	365	368
9	2	348	337
10	0	445	421
10	1	304	213
10	3	398	371

K	L	FOBS	FCAL
11	0	306	216
11	1	290	203
11	2	274	264
12	0	463	488
12	1	383	321

H = 10

K	L	FOBS	FCAL
1	0	499	543
1	1	518	539

K	L	FOBS	FCAL
1	4	273	226
3	0	874	762
3	2	696	736
3	4	543	518
4	3	478	534
5	1	648	663
5	3	394	355
6	2	337	205
7	0	675	717
7	1	344	177

K	L	FOBS	FCAL
7	2	293	277
9	0	614	643
9	1	286	183
10	0	338	378

H = 11.

K	L	FOBS	FCAL
1	0	351	412
3	0	269	282

TABLE A-2

FINAL POSITIONAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS[a] FOR TRIS(HEXACARBONYLDICOBALT-μ-ETHYNYL)ARSINE[c]

ATOM NAME	X	Y	Z	MATRIX LOCATION[b]
As	0.41375(9)	0.40945(7)	0.30002(7)	1-1-2-2
Co1	0.26080(14)	0.25820(9)	0.30318(11)	2-2-4-3
Co2	0.21319(13)	0.27528(9)	0.15026(11)	2-2-3-5
Co3	0.72472(13)	0.39660(10)	0.33223(12)	2-3-5-1
Co4	0.61847(14)	0.39865(10)	0.17547(11)	1-3-1-3
Co5	0.27543(15)	0.56782(9)	0.29661(11)	1-4-4-4
Co6	0.23199(14)	0.54675(9)	0.14499(11)	1-4-5-2
C1	0.2798(11)	0.3427(6)	0.2417(6)	2-5-1-3
C2	0.1571(11)	0.3311(6)	0.2246(7)	2-5-3-4
C3	0.5439(9)	0.3816(6)	0.2585(6)	2-5-2-4
C4	0.6132(10)	0.3274(7)	0.2556(7)	1-5-3-5
C5	0.3506(9)	0.4980(7)	0.2429(7)	1-5-2-5
C6	0.3923(10)	0.5618(6)	0.2365(7)	1-5-1-4
C11	0.2577(12)	0.2961(8)	0.3970(8)	2-3-3-5
O11	0.2588(11)	0.3235(7)	0.4588(7)	2-3-4-2
C12	0.1580(14)	0.1860(8)	0.2957(10)	2-4-4-4
O12	0.0949(11)	0.1390(7)	0.2926(9)	2-4-5-5
C13	0.4231(14)	0.2221(8)	0.3437(9)	2-3-5-4
O13	0.5186(8)	0.2005(5)	0.3680(7)	2-3-1-2
C21	0.1683(13)	0.3281(9)	0.0610(9)	2-1-1-1
O21	0.1388(11)	0.3628(6)	-0.0006(7)	2-1-2-1
C22	0.0877(15)	0.2130(10)	0.1101(11)	2-1-5-5
O22	0.0059(11)	0.1730(7)	0.0815(9)	2-1-1-2
C23	0.3466(12)	0.2282(7)	0.1446(9)	2-1-3-3
O23	0.4328(8)	0.1982(5)	0.1452(7)	2-1-4-3
C31	0.7230(14)	0.3652(10)	0.4277(10)	2-2-3-4
O31	0.7224(11)	0.3399(8)	0.4906(7)	2-2-4-5

TABLE A-2 (CONT'D)

C32	0.8807(14)	0.3612(8)	0.3434(10)	2-2-1-3
O32	0.9712(8)	0.3388(6)	0.3512(8)	2-2-2-3
C33	0.7379(19)	0.4891(14)	0.3519(16)	2-1-2-2
O33	0.7518(17)	0.5463(8)	0.3697(14)	2-1-3-2
C41	0.5023(13)	0.3691(7)	0.0836(9)	1-4-1-1
O41	0.4251(9)	0.3482(6)	0.0214(6)	1-1-4-4
C42	0.7477(16)	0.3692(7)	0.1481(10)	1-4-3-2
O42	0.8280(10)	0.3529(6)	0.1292(8)	1-4-4-1
C43	0.6092(14)	0.4899(10)	0.1565(12)	1-4-1-3
O43	0.6100(11)	0.5518(6)	0.1488(9)	1-4-2-3
C51	0.3902(15)	0.5728(9)	0.3969(10)	1-2-4-3
O51	0.4799(12)	0.5746(8)	0.4626(7)	1-4-2-2
C52	0.2245(12)	0.6600(8)	0.2903(10)	1-1-5-1
O52	0.1917(11)	0.7138(6)	0.2868(9)	1-2-3-1
C53	0.1559(18)	0.5224(8)	0.3128(14)	1-3-2-1
O53	0.0821(14)	0.4888(7)	0.3255(11)	1-3-3-1
C61	0.2812(15)	0.5191(9)	0.0614(10)	1-2-2-4
O61	0.3123(12)	0.5045(7)	0.0092(7)	1-3-5-3
C62	0.1836(12)	0.6364(9)	0.1039(10)	1-2-1-2
O62	0.1605(11)	0.6928(6)	0.0819(9)	1-2-5-4
C63	0.0864(14)	0.5018(8)	0.1166(10)	1-3-1-5
O63	-0.0068(10)	0.4731(6)	0.1020(8)	1-3-2-5

[a] Estimated standard deviations are right justified to the least significant digits of the fractional co-ordinates.

[b] The scale factor was always in matrix one. The numbers correspond to the matrix in which the atom was refined for 1st anisotropic, 2nd anisotropic, 3rd anisotropic and 4th anisotropic cycles respectively. Only arsenic, six cobalts and the acetylenic carbons were anisotropically refined in the 1st anisotropic cycle.

[c] See Figure III-C-1 , page 84 in the text for a description of the numbering scheme used.

TABLE A-3

FINAL THERMAL PARAMETERS[a] ($x10^4$) WITH ESTIMATED STANDARD DEVIATIONS[b]

FOR TRIS(HEXACARBONYLDICOBALT-π-ETHYNYL)ARSINE[c]

ATOM NAME	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
As	62.3(11)	25.4(4)	31.9(6)	5.5(7)	22.8(6)	0.3(5)
Co1	66.8(16)	28.9(7)	52.9(10)	-3.0(10)	31.1(11)	9.9(7)
Co2	70.1(16)	28.7(7)	47.4(10)	-2.9(9)	18.2(10)	-1.1(7)
Co3	56.1(16)	37.2(8)	69.2(12)	0.1(10)	26.0(11)	-9.8(9)
Co4	89.9(18)	23.0(7)	66.3(11)	3.0(10)	54.3(12)	3.2(8)
Co5	107.6(21)	26.4(8)	60.7(11)	11.0(10)	49.4(12)	-0.8(7)
Co6	72.7(18)	24.0(6)	49.2(10)	3.9(9)	25.6(11)	5.2(7)
C1	73(14)	34(5)	26(6)	20(7)	11(8)	6(4)
C2	67(14)	33(5)	38(7)	-12(7)	11(8)	-3(5)
C3	46(12)	31(6)	25(6)	-10(6)	20(7)	-1(4)
C4	21(12)	58(7)	39(7)	19(7)	16(7)	-1(6)
C5	55(12)	32(5)	34(7)	-6(6)	34(7)	-9(5)
C6	108(15)	18(5)	28(6)	9(7)	29(8)	-2(4)

TABLE A-3 (CONT'D)

C11	63(15)	52(6)	43(8)	-10(8)	-18(9)	31(6)
O11	222(18)	94(7)	47(7)	12(8)	50(10)	10(6)
C12	120(20)	46(7)	78(10)	15(9)	39(11)	4(7)
O12	188(16)	79(7)	156(10)	-66(8)	63(10)	30(7)
C13	141(20)	31(6)	52(9)	1(9)	39(12)	22(6)
O13	89(11)	51(5)	106(8)	27(6)	47(8)	22(5)
C21	110(17)	79(9)	42(8)	-23(10)	30(11)	-28(7)
O21	187(17)	81(6)	56(7)	22(18)	36(9)	14(5)
C22	144(22)	62(9)	92(13)	13(11)	20(14)	-18(9)
O22	173(18)	82(8)	142(11)	-46(9)	8(11)	-12(7)
C23	133(18)	16(6)	67(8)	1(7)	15(11)	10(6)
O23	124(12)	42(4)	93(7)	26(6)	27(8)	-9(4)
C31	69(18)	98(11)	43(10)	39(11)	-8(13)	-23(9)
O31	160(15)	138(8)	51(8)	40(8)	27(10)	7(7)
C32	95(8)	52(8)	106(12)	-1(10)	34(13)	11(8)
O32	46(10)	80(6)	152(10)	23(7)	56(9)	5(6)
C33	57(24)	136(16)	156(18)	-20(18)	29(16)	-53(16)
O33	283(26)	68(8)	206(17)	-36(12)	45(15)	-56(10)
C41	122(18)	38(6)	36(8)	13(9)	42(10)	12(6)
O41	175(14)	63(5)	52(7)	-4(7)	50(8)	-5(5)
C42	199(28)	24(5)	90(12)	11(10)	91(15)	14(6)

TABLE A-3 (CONT'D)

O42	210(16)	55(5)	146(10)	31(7)	144(10)	24(6)
C43	157(20)	49(8)	110(14)	9(11)	102(14)	-17(9)
Q43	269(17)	25(4)	162(11)	-3(8)	155(11)	4(6)
C51	249(26)	47(8)	80(11)	58(12)	73(13)	-1(8)
O51	292(21)	97(8)	67(8)	35(11)	24(10)	-13(7)
C52	127(17)	28(6)	102(11)	7(7)	85(11)	-1(7)
O52	286(19)	20(4)	174(11)	18(8)	150(13)	-8(6)
C53	352(33)	4(6)	154(17)	29(10)	148(20)	2(8)
O53	416(26)	38(6)	275(16)	-36(10)	269(17)	-7(8)
C61	127(21)	34(7)	56(10)	8(9)	-7(12)	6(7)
O61	252(19)	85(6)	68(8)	56(8)	79(10)	20(6)
C62	65(14)	55(8)	64(10)	-2(9)	13(9)	-5(8)
O62	200(17)	84(5)	134(10)	20(8)	52(10)	25(6)
C63	152(23)	36(6)	68(11)	27(10)	33(12)	1(6)
O63	111(13)	73(6)	114(9)	-30(8)	9(9)	32(6)

[a] These are applied in the expression $\exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$.

[b] Estimated standard deviations are right justified to the least significant digits of the thermal parameter ($\times 10^4$).

[c] See Figure III-C-1, page 84 in the text for a description of the numbering used.

APPENDIX B

TABLE B-1: The observed and calculated structure factors for μ-bis(diphenylphosphino)methane-μ-diphenylacetylene-tetracarbonyldicobalt.

TABLE B-2: Final positional parameters with estimated standard deviations for μ-bis(diphenylphosphino)methane-μ-diphenylacetylene-tetracarbonyldicobalt.

TABLE B-3: Final thermal parameters ($x10^4$) with estimated standard deviations for μ-bis(diphenylphosphino)-methane-μ-diphenylacetylene-tetracarbonyldicobalt.

TABLE B-4: Equations of planes of the rigid rings in $Co_2(CO)_4\cdot(PhCCPh)(Ph_2PCH_2PPh_2)$

TABLE B-1

K	L	FOBS	FCAL
H = -11			
0	3	134	172
0	5	159	-146
1	2	183	-105
1	3	254	-242
1	4	163	175
1	5	175	-161
1	6	114	-133
2	0	207	-275
2	2	183	199
2	3	149	-118
2	4	263	237
2	6	185	-119
3	0	272	267
3	2	74	83
3	3	212	-207
3	5	298	267
4	0	229	-277
4	1	281	-221
4	2	195	160
4	4	153	-145
4	5	275	237
5	0	91	80
5	2	87	-58
5	3	185	68
5	4	255	-266
6	2	122	181
H = -10			
0	2	715	-696
0	4	214	-206
0	6	134	144
0	8	88	79
1	0	161	-142
1	1	142	118
1	2	198	-198
1	3	428	386
1	4	882	884
1	5	216	-236
1	6	197	185
1	7	186	125
2	0	181	125
2	1	284	273
2	2	146	121
2	3	208	-194
2	4	264	249
2	5	162	-104
2	6	167	-202
2	7	139	-99
2	8	94	-54
3	0	49	16
3	1	186	-176
3	2	159	-167
3	3	473	-422
3	4	419	395
3	6	248	-197
3	7	58	-45
3	8	152	154
4	1	124	136
4	2	281	235
4	3	104	-55
4	4	75	-75
4	5	221	210
4	7	188	148
4	8	93	-100
5	0	105	-120
5	1	210	173
5	3	293	-264
5	4	155	-124
5	5	522	516
5	6	114	-81
5	7	201	-188
5	8	426	-378
6	0	425	-392
6	2	69	46
6	3	135	148
6	4	196	-171
6	6	308	-256
6	7	152	120
7	0	182	-153
7	2	212	194
7	4	276	-265
7	5	140	111
7	6	409	406
8	0	290	271
8	1	225	-245
8	2	90	108
9	0	184	178
9	1	322	-321
9	3	128	136
9	4	94	-147
H = -9			
0	1	352	-341
0	3	1037	994
0	5	73	90
0	7	261	-277
0	9	78	-130
1	0	86	-74
1	1	495	438
1	2	81	23
1	3	351	377
1	4	547	-498
1	5	495	-515
1	9	135	131
1	10	229	-196
2	0	51	-71
2	1	176	-162
2	2	798	-731
2	3	356	-348
2	4	414	369
2	5	116	-110
2	6	73	26
2	8	80	47
2	10	63	23
3	0	101	-82
3	1	216	-237
3	2	417	407
3	3	301	306
3	4	471	432
3	5	288	-262
3	6	108	105
3	7	104	101
3	8	59	51
3	10	123	82
4	0	508	488
4	1	348	329
4	3	413	-402
4	4	85	64
4	5	67	48
4	6	164	-160
4	7	114	-102
4	8	185	-198
4	10	181	-153
5	0	71	-58
5	2	164	-139
5	4	272	263
5	6	376	-379
5	7	182	168
5	9	97	64
5	10	151	113
6	0	245	-248
6	1	607	589
6	2	95	110
6	3	287	-289
6	4	276	-272
6	5	308	278
6	6	129	114
6	7	246	237
6	8	150	-113
6	9	77	-81
7	0	334	-306
7	1	81	84
7	2	103	-124
7	4	133	134
7	5	247	223
7	6	407	-404
7	7	283	-265
7	9	323	-248
8	0	675	-636
8	1	261	-260
8	2	273	250
8	3	58	10
8	4	299	-265
8	5	230	-234
8	6	68	-32
8	7	229	247
8	8	446	394
9	0	240	177
9	2	124	108
9	3	221	-200
9	5	318	-306
9	6	404	371
9	7	202	-186
10	0	226	205
10	1	399	-350
10	2	57	46
10	3	109	136
10	4	219	215
10	6	199	-176
11	1	135	-111
11	2	104	98
11	4	237	-225
11	5	152	-124
12	0	294	285
12	3	174	187
H = -8			
0	2	343	404
0	4	688	-728
0	6	68	-97
0	8	140	205
0	10	440	-427
1	0	100	-76
1	1	170	-160
1	2	544	-572
1	3	251	-234
1	4	403	-424
1	5	298	271
1	6	242	310
1	9	89	102
1	10	108	-111
1	11	263	222
2	0	566	-558
2	2	203	175
2	3	949	944
2	4	153	168
2	5	190	-146
2	6	81	63
2	7	168	-150
2	8	86	73
2	10	175	155
2	11	421	-394
3	0	684	671
3	1	474	456
3	2	53	41
3	3	323	-324
3	4	406	-385
3	5	180	-221
3	6	196	234
3	7	341	-314
3	8	225	202
3	10	190	-168
3	11	239	-203
4	0	96	75
4	1	634	-646
4	2	503	-503
4	3	50	-68
4	4	398	441
4	5	93	-53
4	6	203	172
4	7	180	-153
4	9	185	211
4	10	153	140
4	11	232	187
5	0	107	108
5	1	338	335
5	2	305	351
5	3	350	366
5	4	144	-105
5	5	102	-63
5	6	292	250
5	7	54	-87
5	8	278	-251
5	9	336	331
5	10	134	-145
5	11	217	-187
6	0	514	543
6	1	418	396
6	2	348	-364
6	3	176	-154
6	4	106	74
6	6	236	-254
6	8	459	-457
6	10	63	-112
7	0	593	-589
7	1	110	-124
7	2	168	-225
7	3	132	196
7	4	54	-36
7	5	179	-219
7	6	140	-91
7	7	516	546
7	8	234	-245
7	9	91	54
7	10	322	344

K	L	FOBS	FCAL
8	0	527	-588
8	1	352	375
8	2	150	152
8	3	95	-120
8	4	85	123
8	5	441	478
8	6	180	166
8	9	522	-574
9	0	145	-166
9	1	95	-116
9	4	122	136
9	5	98	-56
9	6	476	-517
9	7	296	-358
9	8	233	285
9	9	275	-304
10	0	98	-138
10	1	94	-146
10	2	268	307
10	3	240	-230
10	4	252	-258
10	5	106	-141
10	6	164	184
10	7	103	72
10	8	347	366
11	0	319	323
11	1	157	-218
11	3	185	-216
11	4	151	149
11	5	423	450
11	6	166	152
11	7	68	-77
12	2	269	288
12	3	178	184
12	4	106	-85
12	6	342	-386
13	0	179	190
13	4	349	-362
13	5	140	191
14	0	185	89
14	2	181	-99

H = -7

K	L	FOBS	FCAL
0	1	191	-128
0	3	552	-547
0	5	152	132
0	7	434	431
0	9	59	-102
0	11	604	526
1	0	224	-189
1	1	164	-188
1	2	392	332
1	3	690	653
1	4	224	-175
1	5	189	157
1	6	313	-297
1	7	88	109
1	8	72	-118
1	9	141	160
1	10	[illegible]	-107
1	11	107	-158
1	12	150	-92
2	0	80	-85
2	1	621	602
2	2	136	99
2	3	49	33
2	4	1036	-933
2	6	754	-756
2	7	338	336
2	8	312	270
2	9	441	-430
2	10	166	-144
2	11	117	-127
2	12	379	339
3	0	650	-672
3	1	1007	-1010
3	2	604	-588
3	3	76	55
3	4	104	103
3	5	631	621
3	6	438	361
3	7	328	-373
3	8	443	444
3	9	179	-158
3	10	346	314
3	11	248	247
3	12	138	78
4	0	89	59
4	1	387	384

K	L	FOBS	FCAL
4	2	717	744
4	3	653	625
4	4	217	197
4	5	137	-126
4	6	120	-122
4	7	951	-962
4	8	552	533
4	9	455	505
4	10	202	-234
4	11	302	-281
4	12	135	-110
5	0	1088	1131
5	1	220	217
5	3	443	-434
5	4	120	-133
5	5	370	-386
5	6	469	443
5	7	318	-331
5	8	163	-202
5	9	146	141
5	10	150	-93
5	12	189	169
6	0	139	-73
6	1	854	-881
6	2	109	-147
6	4	73	93
6	6	273	278
6	7	120	95
6	8	623	-645
6	9	436	434
6	10	209	246
6	11	113	97
7	0	149	160
7	1	498	537
7	2	313	288
7	3	365	376
7	5	214	254
7	7	276	288
7	8	576	-585
7	11	199	-172
8	0	160	168
8	2	378	-378
8	3	121	-140
8	4	248	-257
8	5	69	69

K	L	FOBS	FCAL
8	6	445	-490
8	7	161	171
8	8	327	-411
8	9	105	-125
8	10	216	190
8	11	70	-59
9	0	522	-600
9	1	53	72
9	2	270	-262
9	3	168	170
9	4	309	-350
9	5	177	-156
9	6	242	263
9	7	524	554
9	8	91	80
9	9	112	-133
9	10	60	69
10	0	128	-114
10	1	344	376
10	3	67	-62
10	4	356	360
10	5	127	65
10	6	342	-428
10	7	103	-100
10	9	398	-389
11	0	300	-288
11	1	145	-114
11	2	133	78
11	3	240	-267
11	4	348	400
11	5	622	-687
11	6	536	-565
11	9	61	39
12	2	420	457
12	3	541	-610
12	4	219	-230
12	6	211	186
12	7	290	308
12	8	335	388
13	0	268	300
13	1	271	-302
13	2	64	57
13	3	79	-136
13	4	231	249
13	5	521	589

K	L	FOBS	FCAL
13	7	103	-178
14	0	253	-257
14	1	146	-190
14	2	151	156
14	3	327	378
14	4	279	-309
14	5	158	-169
14	6	89	-116
15	1	81	100
15	2	82	-84
15	4	184	-209

H = -6

K	L	FOBS	FCAL
0	2	574	590
0	4	407	405
0	6	1063	1059
0	8	338	-306
0	12	447	-418
1	0	60	-66
1	1	171	165
1	2	55	132
1	4	142	96
1	5	678	-725
1	6	511	-408
1	7	494	450
1	8	424	404
1	10	288	-265
1	11	235	266
1	12	93	109
1	13	206	198
2	0	969	-896
2	1	73	57
2	2	328	-316
2	6	180	-187
2	7	810	834
2	8	101	-100
2	9	183	-178
2	10	505	512
2	11	195	169
2	12	70	62
2	13	65	-81
3	0	805	-700
3	1	477	485
3	2	580	571

K	L	FOBS	FCAL
3	3	560	537
3	4	229	-197
3	5	440	471
3	6	1038	-1023
3	7	103	-148
3	8	600	632
3	9	367	-325
3	10	60	-15
3	11	365	-335
3	12	246	-232
3	13	176	-137
4	0	893	869
4	1	265	292
4	2	517	-494
4	3	130	-154
4	4	898	-896
4	6	91	-111
4	7	64	-29
4	8	615	584
4	9	531	-477
4	10	255	-225
4	11	253	238
4	12	338	324
4	13	133	119
5	0	684	-728
5	1	1067	-966
5	2	611	-583
5	3	68	26
5	4	571	528
5	5	247	219
5	6	411	418
5	7	767	-715
5	8	253	230
5	9	468	453
5	10	395	379
5	11	240	216
5	12	93	99
5	13	141	-149
6	0	262	238
6	1	149	184
6	2	880	852
6	3	63	46
6	4	73	108
6	6	227	236
6	7	122	-134

K	L	FOBS	FCAL
6	8	241	222
6	9	275	241
6	10	413	-439
6	11	399	-370
6	12	281	-189
7	0	982	898
7	1	441	-414
7	2	268	258
7	3	313	-342
7	4	432	-417
7	5	139	126
7	6	166	169
7	8	680	-566
7	9	135	-143
7	11	237	228
7	12	170	160
8	0	264	-273
8	1	814	-835
8	3	683	574
8	4	227	-258
8	5	193	221
8	6	89	138
8	7	181	30
8	8	225	-246
8	9	335	279
8	10	186	-137
9	0	536	589
9	1	678	699
9	3	662	716
9	4	198	-246
9	6	288	244
9	7	65	100
9	8	112	-151
9	9	287	-234
9	10	154	-131
9	11	219	-174
10	2	786	-771
10	3	257	298
10	5	611	-659
10	6	94	-97
10	7	162	170
10	8	384	-387
10	9	68	65
10	10	170	285
10	11	70	-72

K	L	FOBS	FCAL
11	0	677	-749
11	1	372	398
11	2	79	-93
11	3	158	-190
11	4	102	45
11	5	328	-326
11	6	239	198
11	7	579	603
11	8	140	156
12	0	116	107
12	2	164	171
12	3	213	-223
12	4	[illegible]	806
12	5	221	247
12	6	307	-332
12	7	97	64
12	8	157	-123
12	9	265	-262
13	0	127	126
13	1	425	-455
13	2	377	403
13	5	289	-312
13	6	635	-672
13	7	110	-119
14	0	104	107
14	1	175	158
14	3	297	-291
14	4	159	-137
14	5	181	174
15	0	100	-144
15	1	58	-68
15	3	90	65
15	4	253	319
15	5	98	135
16	0	288	-332
16	2	162	184
16	3	99	-100
16	4	346	-326

H = -5

K	L	FOBS	FCAL
0	1	707	-677
0	3	852	696
0	5	843	-839
0	7	596	-554

K	L	FOBS	FCAL
0	9	416	337
0	11	152	-139
0	13	193	175
1	0	103	174
1	2	314	-290
1	3	984	-865
1	4	51	-16
1	5	727	-663
1	6	1094	1023
1	7	893	820
1	8	97	-159
1	9	403	400
1	11	264	254
1	12	87	89
1	13	121	66
1	14	185	-156
2	0	86	174
2	1	499	-435
2	2	224	242
2	3	247	214
2	4	1088	1014
2	5	225	211
2	6	65	-91
2	7	344	343
2	8	789	-807
2	9	52	61
2	10	86	105
2	11	414	-405
2	12	201	-201
2	13	62	-21
2	14	173	-125
3	0	651	566
3	1	356	402
3	2	395	393
3	3	45	-111
3	4	47	-38
3	5	270	-301
3	6	1305	-1326
3	7	610	-533
3	9	352	-343
3	10	54	-70
3	12	126	76
3	13	292	297
4	0	200	157
4	1	757	-747

K	L	FOBS	FCAL
4	2	1065	-1105
4	3	97	-82
4	4	56	76
4	5	757	756
4	6	42	12
4	7	261	297
4	8	252	272
4	10	469	454
4	11	126	138
4	12	86	-82
4	13	85	-82
5	0	232	-267
5	1	699	729
5	2	198	168
5	3	322	317
5	4	304	283
5	6	374	-391
5	7	347	-359
5	8	553	621
5	9	136	-175
5	10	175	-125
5	11	377	-376
5	12	156	-152
5	13	118	-72
6	0	168	148
6	1	307	314
6	2	182	-125
6	3	820	-868
6	4	64	105
6	5	241	-210
6	6	159	259
6	7	294	-297
6	8	61	-79
6	9	416	-425
6	10	101	70
6	11	382	394
6	12	162	-142
6	13	225	218
7	0	712	-814
7	1	98	-115
7	2	611	667
7	3	353	-382
7	4	85	98
7	5	325	347
7	7	262	-280

K	L	FOBS	FCAL
7	8	164	183
7	9	734	750
7	10	335	400
7	11	283	295
7	12	177	-127
8	0	627	701
8	1	276	321
8	2	800	868
8	3	138	157
8	4	215	-189
8	5	257	254
8	7	118	144
8	9	336	-396
8	10	508	-509
8	12	96	-134
9	0	541	624
9	1	816	-904
9	2	198	-182
9	3	273	263
9	4	682	-754
9	5	55	-48
9	7	37	-16
9	8	401	-380
9	10	128	-90
9	11	356	382
9	12	75	63
10	0	561	-680
10	1	77	91
10	2	153	-97
10	3	590	601
10	4	116	-136
10	5	120	-155
10	6	315	380
10	8	132	106
10	9	466	538
10	10	110	-105
10	11	147	-181
11	0	403	399
11	1	313	364
11	2	413	-447
11	3	274	335
11	4	206	281
11	5	354	-401
11	6	182	220
11	8	132	-152

K	L	FOBS	FCAL
11	9	271	-251
11	11	249	-300
12	0	350	-386
12	1	177	-206
12	2	165	-168
12	3	70	104
12	4	238	258
12	5	679	-724
12	6	225	-262
12	9	205	128
12	10	231	253
13	0	143	174
13	2	228	-303
13	3	216	-197
13	4	164	159
13	6	208	148
13	7	371	346
13	8	392	353
14	0	362	361
14	2	339	-377
14	3	125	120
14	4	520	521
14	5	304	292
14	6	82	-109
14	8	308	-348
15	0	255	-317
15	1	273	267
15	6	287	-311
15	7	58	-89
16	1	174	137
16	2	217	-240
16	3	213	-258
16	5	345	346
16	6	102	141
17	0	290	-304
17	1	132	-163
17	2	225	211
17	3	244	229
17	4	143	169

H = -4

K	L	FOBS	FCAL
0	4	884	-933
0	6	1219	1180
0	8	575	561

K	L	FOBS	FCAL
0	12	83	-118
1	0	142	-156
1	1	648	-644
1	2	448	429
1	3	174	187
1	4	750	759
1	5	624	677
1	6	966	879
1	7	776	-787
1	8	481	-486
1	10	117	-135
1	12	87	-116
1	13	123	-123
1	14	216	-169
2	0	265	262
2	1	266	208
2	2	959	995
2	3	369	415
2	4	45	22
2	5	1267	-1317
2	6	432	-427
2	7	77	-152
2	8	215	-189
2	9	442	451
2	10	194	-139
2	11	91	71
2	12	136	144
2	13	143	121
3	0	302	220
3	1	703	-654
3	2	873	-871
3	3	559	-598
3	4	89	-136
3	5	292	-274
3	6	411	465
3	7	598	639
3	8	73	-64
3	9	107	114
3	10	127	131
3	12	93	67
3	14	313	-321
4	0	711	748
4	1	107	112
4	2	841	-904
4	3	1268	1231

K	L	FOBS	FCAL
4	4	168	190
4	5	170	211
4	6	427	-418
4	7	334	429
4	8	81	-60
4	9	95	135
4	10	76	-95
4	11	509	-517
4	13	183	-195
5	0	140	-152
5	1	533	629
5	2	969	-1066
5	3	539	-587
5	4	373	-398
5	5	376	-420
5	6	445	-533
5	8	136	-195
5	9	282	-287
5	10	327	373
5	11	257	-301
5	12	294	315
5	13	197	224
6	0	782	-892
6	1	253	243
6	2	284	-262
6	3	437	-478
6	4	722	829
6	5	302	346
6	6	83	88
6	7	105	106
6	8	208	237
6	9	257	252
6	10	705	732
6	12	226	-270
6	13	69	40
7	0	167	206
7	1	752	851
7	2	429	515
7	3	142	-250
7	4	365	360
7	8	616	670
7	9	375	-370
7	10	261	-252
7	11	129	-69
7	12	269	-276

K	L	FOBS	FCAL
7	13	113	72
8	0	242	308
8	1	438	-472
8	2	284	244
8	3	961	-1033
8	6	166	-188
8	7	202	-220
8	8	629	-688
8	9	274	-316
8	10	220	214
8	11	615	688
8	13	184	115
9	0	355	-370
9	1	248	-260
9	2	608	671
9	3	334	398
9	4	172	-284
9	5	772	845
9	6	55	-66
9	8	354	361
9	9	818	863
9	11	267	252
9	12	207	-214
10	0	654	712
10	1	341	396
10	2	321	362
10	3	471	508
10	4	512	-581
10	5	136	173
10	7	327	304
10	8	73	83
10	9	584	-601
10	10	489	-555
11	0	114	-116
11	1	298	-379
11	2	551	-622
11	3	194	221
11	4	358	-359
11	5	120	187
11	6	220	234
11	7	258	-250
11	8	416	-458
11	9	69	44
11	10	62	-21
12	0	225	-243

K	L	FOBS	FCAL
12	1	117	-152
12	2	115	-133
12	3	395	418
12	4	143	187
12	5	115	136
12	6	150	116
12	8	547	649
12	10	48	-74
13	0	728	836
13	1	115	-101
13	3	219	225
13	4	258	265
13	5	238	-255
13	6	100	131
13	7	305	-283
13	8	307	-249
13	9	192	-204
13	10	75	-78
14	0	143	202
14	2	98	-82
14	3	109	-115
14	5	568	-587
14	6	183	-149
14	7	294	-290
14	9	461	469
15	0	378	394
15	1	142	197
15	2	174	-191
15	3	485	-542
15	4	270	300
15	5	84	132
15	6	91	168
15	7	423	445
15	8	119	-183
16	0	94	-169
16	1	108	124
16	3	121	106
16	4	117	201
16	5	227	223
16	6	211	-251
16	7	121	-126
17	0	327	-352
17	1	467	474
17	3	186	-185
17	4	403	-429

K	L	FOBS	FCAL
17	6	199	-258
18	0	203	-249
18	1	99	-112
18	2	192	-199
18	3	107	-125

H = -3

K	L	FOBS	FCAL
0	1	865	863
0	3	528	-414
0	5	926	860
0	7	1527	-1538
0	9	480	-465
0	13	376	-395
1	0	1868	-1874
1	1	1118	1149
1	2	637	682
1	3	416	422
1	5	70	34
1	6	68	-36
1	7	566	-638
1	8	256	288
1	9	413	440
1	10	215	237
1	11	309	307
1	12	236	-271
1	13	137	-122
1	14	351	346
2	0	176	-227
2	1	376	-419
2	2	476	-488
2	3	1475	-1695
2	4	655	-742
2	5	529	-562
2	6	1555	1664
2	7	432	482
2	8	160	155
2	9	250	280
2	10	298	-330
2	11	56	20
2	13	166	48
2	14	195	-204
3	0	904	964
3	1	833	-913
3	2	971	1032

K	L	FOBS	FCAL
3	3	717	771
3	4	1003	1153
3	5	411	458
3	6	308	298
3	7	257	-277
3	8	695	-764
3	9	58	-119
3	10	371	-414
3	11	332	376
3	12	113	-158
3	13	253	-284
3	14	256	-247
4	0	24	19
4	1	272	-305
4	2	102	-172
4	3	245	275
4	4	807	-913
4	5	524	-551
4	7	447	535
4	8	82	-68
4	9	184	241
4	10	250	-268
4	11	93	53
4	12	171	173
4	13	99	75
4	14	172	187
5	0	125	-140
5	1	555	630
5	2	982	-1013
5	3	593	636
5	4	135	-171
5	5	206	193
5	6	446	516
5	7	301	-345
5	8	368	-360
5	9	220	198
5	11	282	-300
5	12	358	414
5	13	251	-246
5	14	202	-216
6	0	93	-102
6	1	881	997
6	2	531	-518
6	3	564	635
6	4	617	649

K	L	FOBS	FCAL
6	5	43	-38
6	6	196	-235
6	7	149	176
6	8	272	313
6	9	283	-301
6	11	727	-701
6	13	74	81
7	0	659	-704
7	1	440	507
7	2	249	-357
7	3	831	-711
7	4	685	-769
7	5	956	-1123
7	6	354	359
7	7	176	-173
7	8	228	-332
7	9	422	-437
7	10	678	789
7	12	177	198
7	13	357	334
8	0	561	-591
8	1	392	400
8	2	75	-46
8	3	142	-189
8	4	658	755
8	7	211	-245
8	8	549	579
8	9	217	246
8	10	348	409
8	11	301	282
8	12	362	-417
9	0	614	698
9	1	444	501
9	2	626	739
9	3	254	-291
9	5	194	-202
9	6	174	-159
9	7	531	616
9	9	475	-441
9	10	213	-225
9	11	82	-88
9	12	213	-236
9	13	114	142
10	0	339	-393
10	1	732	-779

K	L	FODS	FCAL
10	2	72	-94
10	3	564	-626
10	4	238	-226
10	5	658	766
10	6	278	-311
10	7	193	-168
[illegible]	8	714	-709
[illegible]	9	67	20
10	11	377	352
10	12	126	187
11	0	745	-852
11	1	148	-151
11	2	390	466
11	3	681	719
11	4	184	-161
11	5	314	342
11	6	597	-625
11	7	380	440
11	8	486	516
11	10	194	151
11	11	171	219
12	0	325	388
12	1	215	227
12	2	166	165
12	3	288	325
12	4	498	-544
12	5	80	75
12	7	134	149
12	8	205	206
12	9	321	-381
12	10	78	-121
13	1	637	-670
13	2	404	-467
13	3	58	119
13	4	369	-406
13	5	113	63
13	7	445	-448
13	8	393	376
13	9	168	155
13	10	135	-180
14	0	392	402
14	1	144	224
14	2	166	-194
14	3	319	323
14	4	184	194

K	L	FOBS	FCAL
14	5	62	-22
14	6	446	488
14	7	63	28
14	9	182	209
14	10	304	-313
15	0	508	504
15	1	115	115
15	2	89	126
15	3	73	-69
15	4	388	412
15	5	77	-121
15	6	200	187
15	7	180	-195
15	8	474	-439
15	9	243	272
16	0	310	326
16	2	140	160
16	3	320	-332
16	4	133	-160
16	5	85	-76
16	6	365	-425
16	7	109	74
17	0	158	144
17	1	54	-30
17	2	187	-197
17	5	307	297
17	6	206	203
18	0	307	-316
18	1	122	100
18	2	190	184
18	3	206	246

H = -2

K	L	FOBS	FCAL
0	2	124	100
0	4	888	747
0	6	1080	-1011
0	8	154	-126
0	10	339	376
0	12	192	-200
0	14	687	540
1	0	1395	-1365
1	1	898	869
1	2	709	-721
1	3	97	46

K	L	FOBS	FCAL
1	4	296	-299
1	6	881	723
1	7	167	-96
1	8	386	399
1	9	462	-368
1	10	293	261
1	11	205	-170
1	12	53	67
1	13	124	102
1	14	101	109
2	0	149	-151
2	1	1103	-1083
2	2	163	-185
2	3	1919	-1789
2	4	331	415
2	5	732	622
2	7	1029	-938
2	8	331	-280
2	9	806	-754
2	10	309	318
2	11	238	176
2	12	270	-245
2	13	343	-297
2	14	177	-172
3	0	898	-795
3	1	1856	-1760
3	2	1138	1125
3	3	859	-755
3	4	526	457
3	5	1457	-1347
3	6	549	-414
3	7	221	258
3	8	355	310
3	9	65	-30
3	10	178	123
3	11	499	443
3	12	350	-356
3	13	368	382
3	14	277	249
4	0	411	-380
4	1	1606	-1509
4	2	696	608
4	3	713	-643
4	4	1068	-930
4	5	1271	1247

K	L	FOBS	FCAL
4	6	959	939
4	7	176	179
4	8	923	490
4	9	82	-57
4	10	769	-789
4	11	547	505
4	12	99	103
4	13	77	-50
4	14	125	-84
5	0	1051	1064
5	1	132	147
5	2	834	-789
5	3	1573	1449
5	4	341	-324
5	5	47	17
5	6	457	-501
5	7	76	-156
5	8	229	-214
5	9	141	84
5	10	561	-537
5	13	632	-557
6	0	425	306
6	1	97	-96
6	2	784	-742
6	3	591	559
6	4	1161	-1095
6	5	58	-125
6	6	347	351
6	7	100	150
6	8	460	-455
6	9	455	421
6	11	500	-392
6	12	592	515
6	13	74	72
7	1	919	834
7	2	1393	-1315
7	4	516	438
7	5	181	-177
7	6	402	-356
7	7	216	199
7	8	478	436
7	9	333	310
7	10	385	430
7	11	235	-334
7	12	109	99

K	L	FOBS	FCAL
7	13	200	-240
8	0	468	-459
8	1	127	167
8	2	345	345
8	3	97	84
8	4	50	102
8	5	892	-794
8	6	646	620
8	8	158	-130
8	9	609	-561
8	10	279	240
8	11	618	-611
8	12	128	-184
8	13	243	229
9	0	95	112
9	1	102	49
9	2	90	56
9	3	1068	-1104
9	4	234	236
9	6	226	166
9	7	371	-417
9	8	224	-150
9	9	75	118
9	10	328	229
9	11	453	393
9	13	285	294
10	0	169	-192
10	1	242	170
10	2	49	80
10	3	305	333
10	4	775	707
10	5	337	-337
10	6	320	-292
10	7	377	352
10	8	325	248
10	9	587	544
10	10	175	154
10	12	379	-296
11	0	357	308
11	1	345	315
11	2	834	774
11	3	334	-295
11	4	305	-332
11	7	912	883
11	8	534	-493

K	L	FOBS	FCAL
11	9	474	-412
11	10	349	-288
11	11	337	-244
12	0	864	-894
12	1	286	-308
12	2	69	8
12	3	148	-167
12	5	661	636
12	6	588	-541
12	8	389	-312
12	9	458	-388
12	10	214	275
12	11	313	275
13	0	474	-438
13	1	315	-326
13	2	211	222
13	3	487	469
13	4	239	-227
13	5	161	208
13	6	458	-421
13	7	137	187
13	8	773	814
13	9	221	-126
14	0	455	501
14	1	63	104
14	2	78	91
14	3	64	101
14	4	204	-175
14	5	178	185
14	6	191	198
14	7	411	-389
14	8	72	162
14	9	151	-163
14	10	279	-245
15	1	428	-406
15	2	226	-164
15	3	160	-172
15	4	213	202
15	5	388	-228
15	6	173	-175
15	7	452	-419
15	8	68	92
15	9	468	387
16	0	197	199
16	2	366	351
16	3	123	-91
16	6	257	204
16	7	161	129
16	8	148	-143
17	0	336	366
17	2	189	155
17	3	153	148
17	4	160	229
17	5	184	187
17	7	154	-188
18	0	199	208
18	2	189	-210
18	3	64	-68
18	4	315	-292
18	5	197	-176
19	0	319	-334
19	2	269	-249
19	3	199	147

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K	L	FOBS	FCAL
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0	7	220	-177
0	9	908	981
0	11	418	-414
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1	1	2461	2574
1	2	1538	-1488
1	3	1004	967
1	4	1013	940
1	5	145	-80
1	6	374	-339
1	7	254	297
1	8	722	-725
1	9	453	-438
1	10	249	282
1	11	393	-405
1	12	101	115
1	13	253	-238
1	14	77	122
2	0	1786	-1599
2	1	474	536
2	2	1149	-1132
2	3	142	107
2	4	1563	-1418
2	5	1145	-1076
2	6	114	-114
2	7	409	356
2	8	125	186
2	9	350	-385
2	10	745	754
2	11	106	-126
2	12	216	-196
2	13	207	198
2	14	293	284
3	0	1095	-1081
3	1	1191	1135
3	2	105	77
3	3	1026	-934
3	4	960	882
3	5	1322	1333
3	6	1335	1313
3	7	356	356
3	8	515	467
3	9	858	-835
3	10	131	104
3	11	144	123
3	12	169	-175
3	13	255	273
3	14	324	-342
4	0	622	-603
4	1	1785	-1749
4	2	1369	1423
4	3	1062	859
4	4	856	730
4	5	513	-495
4	6	440	-390
4	7	640	-591
4	8	86	79
4	9	396	-432
4	10	220	-241
4	11	596	556
4	12	620	-580
4	13	161	-135
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5	1	112	-168
5	2	1042	1005
5	3	749	-718
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5	5	1174	-1134
5	6	143	-117
5	7	130	109
5	8	790	739
5	9	248	250
5	10	716	-675
5	11	268	298
5	13	163	126
5	14	472	457
6	0	683	786
6	1	551	-578
6	2	692	-769
6	3	1220	1142
6	4	613	622
6	5	1074	1068
6	6	510	433
6	7	518	522
6	8	299	-252
6	10	438	-411
6	11	405	391
6	12	412	345
6	13	494	-487
6	14	68	-33
7	1	535	-527
7	2	98	-146
7	3	1470	1379
7	4	737	-728
7	5	241	191
7	6	1066	-1043
7	7	564	-568
7	11	673	-653
7	12	100	-138
7	13	534	-527
8	0	417	379
8	1	263	226
8	2	900	-832
8	3	398	-369
8	4	681	-678
8	5	392	-351
8	7	137	-154
8	8	490	472
8	9	318	334
8	11	405	-415
8	12	460	447
8	13	95	121
9	0	654	546
9	1	395	-387
9	2	1140	-1067
9	3	382	375
9	4	251	294
9	5	445	372
9	6	505	498
9	7	270	-263
9	8	236	257
9	9	90	-84
9	10	191	189
9	11	64	-91
9	12	110	-68
10	0	613	690
10	1	46	110
10	3	168	176
10	5	775	-764
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10	7	402	-375
10	8	659	-578
10	9	232	-255
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11	0	220	-154
11	1	198	208
11	2	570	-525
11	3	754	-767
11	4	614	585
11	5	198	-162
11	6	211	-213
11	8	642	-623
11	9	618	561
11	10	109	106
11	11	481	398
11	12	143	105
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12	2	414	424
12	4	459	413
12	6	479	~~-479~~
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12	9	227	191
12	10	194	125
12	11	269	-231
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13	2	269	247
13	3	474	-486
13	4	281	-344
13	5	416	389
13	7	495	432
13	8	258	-312
13	9	449	-407
14	0	490	-473
14	1	243	-274
14	2	450	-498
14	3	92	69
14	4	116	141
14	5	192	221
14	6	501	-468
14	7	309	-324
14	8	343	296
14	10	180	177
15	0	247	-231
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15	2	349	339
15	4	87	124
15	5	133	-122
15	6	101	116
15	7	112	108
15	8	452	441
16	0	473	434
16	1	128	170
16	2	133	141
16	3	444	-414
16	4	92	86
16	5	288	250
16	6	184	186
16	7	347	-354
17	1	407	-375
17	2	154	229
17	3	133	-124
17	4	153	-162
17	5	135	-126
17	7	191	-166
18	1	208	-203
18	2	231	215
18	3	68	128
18	5	185	165
19	0	249	256
19	1	149	143

K	L	FOBS	FCAL
19	3	378	348

H = 0

K	L	FOBS	FCAL
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0	4	352	-427
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0	10	892	-963
0	12	120	126
0	14	251	286
1	2	2363	-2651
1	3	134	132
1	4	262	341
1	5	294	341
1	6	139	229
1	7	315	-335
1	8	951	-987
1	9	622	663
1	10	327	384
1	11	109	-144
1	12	316	349
1	14	326	340
2	1	2258	2477
2	2	148	-230
2	3	577	-607
2	4	276	378
2	5	153	-168
2	6	159	168
2	7	158	194
2	8	73	71
2	9	98	-78
2	10	322	359
2	11	744	-792
2	12	148	145
2	13	181	-154
2	14	167	-157
3	1	918	907
3	2	818	842
3	3	324	387
3	4	371	-355
3	5	61	122
3	6	367	-281
3	7	74	-94
3	8	474	-588

K	L	FOBS	FCAL
3	9	787	-813
3	10	772	785
3	12	277	-285
3	14	125	-115
4	0	1915	-2024
4	1	252	296
4	2	1152	-1007
4	3	2011	-2039
4	5	629	-632
4	6	265	-290
4	8	487	487
4	9	133	-186
4	10	323	304
4	11	169	219
4	12	195	-193
4	13	602	563
5	1	305	-455
5	2	1544	1476
5	3	641	562
5	4	1564	1600
5	5	188	132
5	6	479	462
5	7	283	258
5	8	112	89
5	9	379	-420
5	10	251	-232
5	11	489	956
5	14	355	-372
6	0	585	-635
6	2	1289	1237
6	3	671	-600
6	4	44	32
6	5	353	-299
6	6	564	-990
6	7	72	120
6	8	232	-256
6	9	147	198
6	10	108	-96
6	12	435	-472
6	13	156	-205
7	3	1236	-1131
7	4	792	-838
7	5	814	802
7	7	784	711
7	8	388	354

K	L	FOBS	FCAL
7	10	392	-386
7	12	368	370
7	13	81	94
8	0	280	-257
8	1	1348	-1286
8	2	389	-645
8	3	960	886
8	4	385	362
8	5	1370	1337
8	7	187	-168
8	8	219	192
8	9	232	-287
8	10	225	194
8	11	226	289
8	12	157	179
8	13	438	-262
9	3	766	761
9	4	152	-211
9	5	573	-575
9	6	322	-350
9	7	904	-839
9	8	254	227
9	11	549	-440
9	12	190	198
9	13	272	-260
10	0	415	84
10	1	370	294
10	2	932	-995
10	3	397	-522
10	4	269	-273
10	5	314	-296
10	6	886	886
10	7	393	-389
10	8	380	381
10	9	340	299
10	10	86	-90
10	11	72	101
10	12	186	202
11	1	119	141
11	3	397	386
11	4	328	333
11	5	370	-401
11	6	554	588
11	7	55	37
11	8	222	-219

K	L	FOBS	FCAL
11	9	192	222
11	11	181	-123
11	12	199	-179
12	0	534	506
12	1	271	238
12	3	112	-134
12	5	453	-400
12	6	190	259
12	7	303	275
12	8	709	-710
12	10	385	-293
13	1	281	-406
13	2	566	-582
13	4	81	107
13	6	543	-533
13	7	94	180
13	8	309	-296
13	9	165	167
13	10	94	110
13	11	265	268
14	1	481	557
14	5	64	-100
14	6	154	-157
14	7	587	573
14	8	127	189
14	9	122	-129
14	10	81	-80
15	1	549	525
15	2	686	-624
15	5	187	225
15	7	114	-96
15	8	100	-38
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16	1	71	-98
16	4	412	338
16	6	523	-504
16	7	90	-107
16	8	316	270
17	1	187	239
17	2	314	492
17	3	170	-223
17	6	220	261
18	0	279	-267
18	2	358	397

K	L	FOBS	FCAL
18	3	97	-120
18	5	195	256
19	1	187	-179
19	2	132	126

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K	L	FOBS	FCAL
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0	7	134	-182
0	9	811	832
0	11	892	909
0	13	122	128
1	1	312	192
1	2	460	512
1	4	136	138
1	5	203	198
1	6	153	-105
1	7	179	-73
1	8	581	654
1	9	1115	1207
1	10	615	-669
1	11	269	-291
1	13	341	-338
2	0	1818	1899
2	1	638	576
2	2	1021	977
2	3	455	-452
2	4	663	691
2	5	162	182
2	6	182	248
2	7	236	174
2	8	928	-1001
2	10	191	-227
2	11	387	-378
2	12	142	156
2	13	193	-203
2	14	162	147
3	0	1104	-1081
3	1	738	734
3	2	538	511
3	3	1576	1434
3	4	894	-866
3	5	864	-790

K	L	FOBS	FCAL
3	6	263	-364
3	7	337	-375
3	8	245	-275
3	9	465	491
3	10	672	699
3	11	156	-121
3	12	377	437
3	14	78	86
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4	1	942	884
4	2	515	-489
4	3	246	289
4	4	901	813
4	5	336	276
4	6	683	664
4	7	478	476
4	8	237	263
4	9	792	-820
4	10	155	190
4	12	74	105
4	13	228	-301
4	14	233	-231
5	0	733	685
5	1	141	-181
5	2	364	-292
5	3	90	97
5	4	819	825
5	5	940	-911
5	6	188	-186
5	7	609	-600
5	8	347	-385
5	9	81	-93
5	10	127	167
5	12	167	-167
5	13	61	-79
5	14	119	-155
6	0	697	-786
6	1	555	514
6	2	183	135
6	3	1247	-1252
6	4	607	515
6	5	807	-694
6	6	217	250
6	7	501	459
6	8	232	205

K	L	FOBS	FCAL
6	9	228	223
6	10	312	-296
6	11	282	155
6	12	251	244
6	13	557	596
7	1	211	182
7	2	321	-342
7	3	93	69
7	4	1216	1192
7	5	964	966
7	6	136	-153
7	7	732	697
7	8	241	-187
7	9	288	-327
7	11	403	369
7	12	273	-231
7	13	149	187
8	0	423	-379
8	1	704	609
8	2	962	879
8	4	388	-311
8	5	483	407
8	6	1310	-1294
8	7	419	-387
8	8	82	147
8	9	120	-159
8	10	271	-329
8	11	252	-192
8	12	431	-378
9	0	655	546
9	2	758	-721
9	3	863	-640
9	4	918	-848
9	5	547	572
9	7	115	126
9	8	778	882
9	9	132	-107
9	10	514	-508
9	11	216	214
9	12	142	177
10	0	605	-690
10	1	436	-425
10	2	449	-342
10	3	426	459
10	5	567	537

K	L	FOBS	FCAL
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10	7	622	-601
10	8	381	343
10	10	134	182
11	0	284	-154
11	1	769	803
11	2	958	959
11	3	364	-458
11	4	364	-397
11	5	544	-580
11	6	231	235
11	7	656	-402
11	8	184	-173
11	9	214	173
11	11	269	-332
11	12	197	144
12	0	412	411
12	1	727	-678
12	3	432	-449
12	4	316	-277
12	5	44	23
12	6	298	227
12	10	261	205
12	11	378	303
13	1	604	-625
13	2	504	493
13	3	870	821
13	6	310	216
13	7	271	241
13	9	81	62
14	0	480	473
14	2	223	-317
14	3	305	317
14	4	331	-335
14	7	132	-173
14	8	287	-217
14	9	62	74
14	10	383	-381
15	0	187	-231
15	2	863	-879
15	3	382	396
15	4	98	145
15	5	405	-435
15	6	208	-194
15	7	164	202

K	L	FOBS	FCAL
15	9	250	263
16	0	463	-434
16	1	639	618
16	4	69	114
16	5	126	-178
16	6	111	124
16	7	371	369
17	3	273	-277
17	4	345	342
17	5	116	118
17	6	266	-247
17	7	242	-212
18	1	113	-84
18	2	268	286
18	3	174	-177
18	5	64	-49
19	0	251	256
19	1	182	162
19	2	118	125
19	3	259	-222

H = 2

K	L	FOBS	FCAL
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0	14	70	-77
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1	1	90	102
1	2	1672	1644
1	3	1668	-1767
1	4	282	-284
1	6	367	411
1	7	413	-454
1	8	718	-799
1	10	430	-486
1	11	168	167
1	13	175	171
1	14	123	153
2	0	150	-151
2	1	1694	-1611
2	2	1374	1369

K	L	FOBS	FCAL
2	3	1008	-1013
2	4	442	385
2	5	433	399
2	6	956	-988
2	7	445	-491
2	8	183	-194
2	9	859	930
2	10	250	250
2	11	289	294
2	14	131	107
3	0	891	795
3	1	555	474
3	2	1178	1127
3	3	388	345
3	4	782	-753
3	5	1104	1076
3	6	300	270
3	7	487	524
3	8	307	302
3	9	54	24
3	10	217	-261
3	11	245	-205
3	13	224	-270
3	14	113	115
4	0	406	-360
4	1	279	245
4	2	387	-381
4	3	860	836
4	4	965	-894
4	5	47	75
4	6	95	98
4	7	819	-844
4	8	852	-844
4	9	427	-454
4	12	211	199
4	13	297	-270
5	0	1049	-1084
5	1	600	-484
5	2	285	-228
5	3	112	172
5	4	961	-850
5	5	1130	-1051
5	6	604	625
5	8	433	435
5	9	422	452

K	L	FOBS	FCAL
5	10	382	358
5	12	301	268
6	0	426	386
6	1	753	609
6	2	436	-420
6	3	84	115
6	4	901	921
6	5	524	-480
6	6	902	838
6	7	262	228
6	8	166	-149
6	9	185	-177
6	10	83	-129
6	12	167	166
6	13	143	162
7	1	226	-201
7	2	156	182
7	3	80	-151
7	4	1175	1143
7	5	893	-912
7	6	291	-294
7	7	155	130
7	8	455	-350
7	9	237	-231
7	11	393	-354
7	13	417	382
8	0	466	-459
8	1	69	85
8	2	480	-411
8	3	805	-841
8	4	296	272
8	6	388	-377
8	7	785	769
8	8	465	472
8	10	135	-175
8	11	209	230
8	12	223	204
9	0	98	-112
9	1	229	-154
9	2	211	-208
9	3	797	763
9	4	806	737
9	5	1184	1115
9	6	442	-445
9	7	430	383

K	L	FOBS	FCAL
9	8	63	-49
9	10	338	293
9	11	186	-101
9	12	235	-285
10	0	183	-192
10	1	1160	1101
10	2	356	343
10	4	486	-463
10	6	655	-671
10	7	482	-476
10	8	327	336
10	9	251	232
10	11	494	-491
11	0	354	-308
11	1	543	495
11	2	943	-913
11	3	765	-805
11	4	117	-146
11	5	129	183
11	7	55	-92
11	8	330	337
11	9	221	-214
11	11	215	184
12	0	860	-894
12	1	261	-245
12	2	1057	1049
12	3	121	134
12	4	205	149
12	5	531	579
12	6	288	286
12	7	393	-414
12	8	6	2
12	9	115	95
12	10	222	249
12	11	189	-135
13	0	482	430
13	1	201	187
13	2	770	784
13	3	361	-316
13	4	694	-683
13	6	85	-87
13	7	501	-542
13	8	74	107
13	9	74	-31
13	10	347	-319

K	L	FOBS	FCAL
14	0	501	501
14	1	1124	-1203
14	2	465	-399
14	3	280	277
14	4	446	-415
14	6	275	245
14	8	180	-120
14	9	194	181
15	3	727	709
15	4	97	-85
15	5	64	33
15	6	352	357
15	7	121	149
15	8	188	-137
16	0	187	199
16	1	87	68
16	2	616	-621
16	4	78	22
16	6	80	-93
17	0	344	-366
17	3	146	80
17	4	61	-98
17	5	292	-252
17	6	118	-122
18	1	307	284
18	3	281	-233
18	4	73	62
18	5	320	334
19	1	115	-195
19	2	117	-172

H = 3

K	L	FOBS	FCAL
0	1	1302	-1057
0	3	573	-469
0	5	572	-418
0	7	64	69
0	9	277	-306
0	11	266	298
1	0	2069	-1978
1	1	1846	1858
1	2	2307	-2193
1	3	1051	-949
1	4	1499	1348
1	6	287	-296

K	L	FOBS	FCAL
1	7	584	-640
1	9	506	522
1	10	129	-109
1	11	306	278
1	13	256	254
2	0	209	227
2	1	506	501
2	2	1917	1726
2	3	1552	-1460
2	4	1593	1479
2	5	109	139
2	6	119	67
2	7	737	753
2	8	436	448
2	10	364	-282
2	11	164	-150
2	12	339	-362
3	0	1093	986
3	1	973	-912
3	2	1236	1148
3	3	1400	-1350
3	4	437	-416
3	5	1072	1044
3	6	452	-537
3	7	467	-434
3	8	591	-639
3	9	312	-306
3	10	54	-36
3	11	284	289
3	12	102	-118
3	13	55	-34
4	0	32	-18
4	1	482	435
4	3	843	655
4	4	1021	-963
4	5	288	212
4	6	139	183
4	7	693	-669
4	8	739	756
4	9	818	838
4	10	224	265
4	11	180	159
4	13	304	-301
5	0	182	-140
5	1	1056	987

K	L	FOBS	FCAL
5	2	220	-115
5	3	280	282
5	4	903	-898
5	5	531	496
5	6	1310	1210
5	8	66	84
5	9	276	-232
5	10	361	-359
5	11	139	-182
5	12	62	62
5	13	235	-190
6	0	119	102
6	1	164	148
6	2	220	-253
6	3	679	621
6	4	62	-80
6	5	412	-384
6	6	278	269
6	7	986	-921
6	8	638	-624
6	10	114	-134
6	11	120	-122
6	12	192	228
6	13	78	-71
7	0	782	-704
7	1	174	-168
7	2	448	416
7	3	120	-88
7	4	247	233
7	5	979	-953
7	6	358	371
7	7	187	141
7	8	237	226
7	9	346	337
7	11	258	254
7	12	178	203
8	0	594	592
8	1	265	-215
8	2	198	231
8	3	384	366
8	4	86	111
8	5	261	-207
8	6	364	341
8	7	176	287
8	8	357	-378

K	L	FOBS	FCAL
8	9	138	140
8	12	305	-273
9	0	719	691
9	1	26	-5
9	2	386	433
9	3	532	569
9	4	127	148
9	5	374	-338
9	6	671	-662
9	7	78	-39
9	8	104	-128
9	9	194	193
9	10	183	-166
9	11	387	-355
9	12	62	49
10	0	397	394
10	1	206	201
10	2	1355	-1297
10	3	232	-207
10	4	308	-284
10	5	102	163
10	7	605	566
10	8	121	92
10	9	275	-260
10	10	243	215
10	11	74	-47
11	0	853	-853
11	1	464	409
11	3	277	276
11	4	576	598
11	5	707	713
11	7	298	-337
11	9	159	-96
11	10	759	675
11	11	334	-301
12	0	371	-385
12	1	945	972
12	2	506	530
12	3	515	-550
12	4	134	-127
12	5	214	-181
12	6	346	-310
12	7	141	-148
12	8	489	433
12	9	355	-278

K	L	FOBS	FCAL
12	10	215	187
13	1	536	-511
13	2	125	-97
13	3	684	-638
13	4	181	-165
13	5	250	239
13	6	222	212
13	9	304	-304
14	0	449	-402
14	1	543	-484
14	2	902	848
14	3	230	250
14	4	175	173
14	5	466	431
14	8	143	-108
15	0	571	584
15	1	83	-98
15	2	219	256
15	4	266	-264
15	5	60	98
15	6	259	-243
15	7	115	80
15	8	181	-174
16	0	338	-326
16	1	730	-746
16	2	113	-111
16	3	209	165
16	4	327	-368
16	6	206	-162
16	7	195	143
17	0	164	148
17	1	374	360
17	3	138	122
17	4	317	-303
17	5	209	182
18	0	338	316
18	1	176	-232
18	2	507	-463
18	3	175	204

H = 4

K	L	FOBS	FCAL
0	0	1452	-1242
0	2	1597	-1498
0	4	737	-659
0	6	439	361
0	8	75	78
0	10	193	169
0	12	251	250
1	0	147	157
1	1	425	470
1	2	1165	-994
1	3	1367	1272
1	4	439	418
1	5	643	-688
1	6	76	84
1	7	109	119
1	8	538	555
1	9	304	-317
1	10	184	-196
1	11	277	-293
1	12	68	-91
2	0	224	164
2	1	75	94
2	2	780	-672
2	3	1493	-1459
2	5	618	-769
2	6	255	281
2	7	75	44
2	8	771	-762
2	9	186	-189
2	13	432	412
3	0	344	-220
3	1	271	237
3	2	611	507
3	3	816	-808
3	4	256	281
3	5	214	205
3	6	1039	-1026
3	7	212	213
3	8	257	258
3	9	573	611
3	10	436	418
3	11	252	268
3	12	265	-265
4	0	826	750
4	1	212	-192
4	2	1155	1034
4	4	368	-313
4	5	178	184

K	L	FOBS	FCAL
4	6	129	168
4	7	995	918
4	8	182	187
4	9	464	-396
4	10	225	-244
4	12	322	-326
5	0	180	197
5	1	39	14
5	2	135	-154
5	3	678	-598
5	4	357	-480
5	5	947	939
5	6	464	-472
5	7	731	-769
5	8	378	-373
5	9	358	-319
5	11	184	128
5	12	158	162
6	0	922	-893
6	1	28	35
6	3	571	582
6	4	213	-284
6	5	328	-272
6	6	311	-279
6	7	222	-222
6	8	928	922
6	9	311	279
6	10	278	265
6	11	152	168
6	12	162	128
7	0	197	-207
7	1	137	-108
7	2	687	743
7	3	94	-107
7	4	728	-690
7	5	116	-98
7	6	757	779
7	8	188	84
7	9	199	-229
7	10	92	-72
7	11	108	-67
8	0	292	308
8	1	730	-767
8	2	73	104
8	3	135	-108
8	4	462	458
8	5	278	-267
8	6	68	-48
8	7	598	-592
8	8	158	-164
8	10	349	-346
9	0	414	378
9	1	747	-731
9	2	82	49
9	3	586	461
9	4	143	-154
9	5	258	-274
9	6	367	378
9	7	267	246
9	8	172	-188
9	9	388	366
9	10	159	-128
9	11	481	355
10	0	762	712
10	1	157	166
10	2	421	-399
10	3	383	408
10	4	341	284
10	5	574	563
10	7	119	112
10	8	515	-494
10	9	587	540
11	0	134	116
11	1	786	744
11	2	462	-433
11	5	444	-395
11	6	336	-327
11	7	231	244
11	8	287	-261
11	9	208	159
11	10	73	-21
12	0	262	-243
12	1	213	226
12	2	412	-405
12	3	644	-602
12	4	121	-108
12	5	234	240
12	6	364	343
12	7	195	228
12	8	354	-321
12	9	381	-382
13	0	836	-837
13	1	236	273
13	2	255	278
13	3	166	179
13	4	488	472
13	5	113	-93
13	6	148	113
13	7	273	-199
13	8	168	179
13	9	156	-158
14	0	158	202
14	1	429	482
14	2	484	432
14	3	347	-331
14	5	584	-539
14	6	158	158
14	7	106	151
14	8	222	187
15	0	420	-394
15	1	521	-491
15	2	371	378
15	3	280	-275
15	4	163	121
15	6	126	89
15	7	185	207
16	0	129	-169
16	1	132	120
16	2	512	488
16	3	195	195
16	5	144	166
16	6	245	-231
17	0	376	362
17	1	269	-294
17	3	94	97
17	4	315	-264
18	0	235	-250
18	1	358	-325
18	2	327	-294
H = 5			
0	3	1680	1866
0	5	765	833
0	7	163	-180
0	9	185	-186
0	11	123	-123
1	0	189	173
1	1	401	408
1	2	287	-253
1	3	189	244
1	4	960	-1018
1	5	967	-927
1	6	412	443
1	7	336	-353
1	10	198	-209
1	11	205	-212
1	12	380	412
2	0	88	-175
2	1	188	165
2	2	1263	-1334
2	3	83	-86
2	4	626	678
2	5	532	-474
2	6	493	473
2	7	164	-146
2	8	95	76
2	9	339	345
2	10	242	269
2	12	163	133
3	0	668	568
3	1	441	-427
3	2	80	138
3	3	232	-186
3	4	388	364
3	5	450	-431
3	6	257	216
3	7	542	584
3	11	396	-421
3	12	449	-462
4	0	203	-160
4	1	347	273
4	2	321	300
4	3	797	-836
4	4	152	184
4	6	55	-63
4	7	166	-188
4	8	666	-654
4	10	79	60
4	11	167	169
5	0	254	-267
5	1	552	-509
5	3	62	-24
5	4	111	135
5	6	520	-570
5	7	580	620
5	8	362	393
5	9	221	264
5	10	190	188
6	0	175	-149
6	1	685	655
6	2	252	239
6	3	492	479
6	4	653	-647
6	5	607	611
6	7	490	491
6	9	504	-529
6	10	117	67
6	11	135	-142
7	0	818	-815
7	1	253	-225
7	2	419	-330
7	3	203	151
7	4	162	166
7	5	227	214
7	6	446	-425
7	7	793	-762
7	8	87	-89
7	9	371	-366
7	10	147	137
7	11	105	117
8	0	735	-703
8	1	336	-321
8	2	721	735
8	3	146	155
8	4	387	-370
8	5	715	-720
8	7	83	87
8	8	702	664
8	9	197	-161
8	10	98	94
8	11	225	243
9	0	628	625
9	1	488	-465
9	2	350	362
9	3	295	-289
9	4	177	135
9	5	313	279
9	6	552	546
9	7	270	-267
9	8	147	137
9	10	433	-417
10	0	673	681
10	1	824	-811
10	2	129	-128
10	3	290	275
10	4	129	154
10	5	306	-325
10	6	275	-283
10	7	472	-450
10	9	183	196
10	10	486	-492
11	0	469	400
11	2	248	-193
11	3	176	207
11	4	319	-299
11	6	174	175
11	7	280	251
11	8	270	-266
11	9	469	471
12	0	403	387
12	1	480	493
12	2	305	-287
12	3	164	176
12	4	147	119
12	5	527	451
12	6	106	-87
12	7	101	121
12	8	160	-147
13	0	*169	174
13	1	344	339
13	2	264	-260
13	3	180	171
13	4	453	-438
13	5	226	-307
13	7	189	153
14	0	416	-362
14	2	242	-261
14	3	121	-119
14	6	422	438

K	L	FOBS	FCAL
14	7	82	-91
15	0	384	-317
15	1	469	425
15	2	385	349
15	4	521	515
15	5	451	-413
15	6	160	-151
16	2	237	259
16	3	578	-510
16	4	76	100
17	0	337	-304
17	1	468	-423

H = 6

K	L	FOBS	FCAL
0	0	768	656
0	2	784	843
0	4	1020	-1023
0	6	719	-795
0	8	196	176
0	10	453	-502
1	0	59	-66
1	1	556	-566
1	2	1365	-1354
1	3	899	940
1	4	250	-288
1	5	795	829
1	6	279	312
1	7	48	34
1	8	324	347
1	9	125	-134
1	10	59	-28
1	11	270	-278
2	0	953	-980
2	1	143	-131
2	2	441	434
2	3	857	857
2	4	84	121
2	5	338	-384
2	6	55	108
2	7	331	-354
2	11	550	-606
3	0	787	782
3	1	78	27
3	2	275	-247
3	3	654	-663
3	4	305	-308
3	5	107	-111
3	6	152	158
3	7	219	-241
3	10	204	-214
3	11	232	-229
4	0	873	873
4	1	1267	-1216
4	2	509	-515
4	3	63	-30
4	4	561	530
4	5	136	-197
4	6	50	99
4	7	117	-134
4	8	237	305
4	9	392	417
4	10	132	129
4	11	244	224
5	0	675	730
5	1	191	177
5	2	597	560
5	3	101	-106
5	4	437	438
5	5	236	-235
5	6	205	197
5	7	146	161
5	8	628	-644
5	9	251	259
5	10	353	-373
5	11	235	-239
6	0	267	238
6	1	222	249
6	2	135	-182
6	3	491	-502
6	4	40	28
6	5	54	-19
6	6	391	-426
6	7	167	142
6	8	408	-433
6	9	213	245
6	10	342	355
7	0	950	-908
7	1	157	196
7	2	241	-216
7	3	60	-36
7	5	71	-68
7	6	192	-184
7	7	529	562
7	8	186	142
7	10	440	460
8	0	283	-273
8	1	609	572
8	2	91	82
8	3	204	-231
8	4	129	-172
8	5	488	503
8	6	149	102
8	7	285	218
8	8	143	124
8	9	597	-626
9	0	574	-590
9	1	402	-475
9	2	209	214
9	3	114	-85
9	4	231	226
9	5	245	-225
9	6	348	-342
9	7	505	-555
9	8	183	206
9	9	345	-345
10	1	228	-189
10	2	358	381
10	3	98	-94
10	4	249	-272
10	5	345	-325
10	6	210	215
10	8	392	409
10	9	108	115
11	0	741	758
11	2	61	-85
11	3	289	-264
11	4	325	318
11	5	352	347
11	6	174	161
11	7	141	-162
11	8	94	-84
12	0	117	107
12	1	547	-556
12	2	168	-188
12	3	126	127
12	5	153	-163
12	6	229	-257
13	0	156	-127
13	1	113	-107
13	2	33	8
13	3	104	110
13	4	379	-410
13	5	224	211
13	6	243	215
14	0	114	106
14	1	470	419
14	2	105	-153
14	3	561	494
14	5	108	-79
15	0	117	145
15	1	320	240
15	2	299	-301
15	3	82	89
15	4	278	-216
16	0	334	-332
16	2	232	-211

H = 7

K	L	FOBS	FCAL
0	1	213	-217
0	3	21	10
0	5	857	867
0	7	492	536
0	9	260	-262
1	0	221	-188
1	1	147	-168
1	2	958	994
1	3	1032	1019
1	4	288	-303
1	5	184	234
1	6	348	-349
1	8	86	-73
1	9	241	193
2	0	89	86
2	1	571	583
2	2	236	-257
2	3	475	-473
2	4	566	-571
2	6	231	-195
2	7	90	114
2	8	248	235
2	9	206	-188
2	10	477	-495
3	0	646	-676
3	1	472	-517
3	2	568	-569
3	3	229	236
3	4	331	300
3	5	436	475
3	6	280	218
3	7	117	94
3	8	211	203
3	9	203	-186
3	10	438	438
4	0	94	-60
4	1	273	-306
4	2	711	752
4	3	203	201
4	4	152	-143
4	5	74	-88
4	7	723	-722
4	8	346	387
4	9	143	153
4	10	200	-235
5	0	1145	1134
5	1	441	-440
5	2	397	-392
5	3	267	-305
5	5	345	-346
5	6	195	210
5	7	158	-139
5	9	111	151
6	0	156	73
6	1	353	-357
6	2	304	-268
6	3	136	122
6	4	205	224
6	5	47	-21
6	6	467	461
6	7	187	176
6	8	220	-221
6	9	658	605
7	0	168	161
7	1	698	687
7	2	209	187
7	3	81	-43
7	5	102	110
7	6	103	-70
7	7	309	290
7	8	550	-552
7	9	127	-100
8	0	180	-167
8	1	53	44
8	2	389	-384
8	3	61	-61
8	6	331	-341
8	7	91	80
8	8	265	-267
9	0	576	-601
9	1	146	132
9	2	113	94
9	4	261	-225
9	5	96	-81
9	7	225	205
9	8	430	430
10	0	146	114
10	1	179	176
10	2	176	-163
10	3	214	-235
10	4	356	343
10	5	130	99
10	6	~~217~~	207
10	7	72	-86
11	0	331	-288
11	1	267	-216
11	4	355	353
11	5	283	-322
11	6	307	-303
11	7	193	-204
12	1	59	51
12	2	429	400
12	3	394	-413
12	4	135	-148
12	5	304	307
12	6	105	-97
13	0	300	301
13	1	158	-138
13	2	152	116
13	3	163	155

K	L	FOBS	FCAL
13	4	134	-147
13	5	469	462
14	0	279	259
14	1	125	-178
14	2	85	72
14	3	174	153
14	4	603	-546
15	2	296	-293

H = 8

K	L	FOBS	FCAL
0	0	62	-43
0	2	747	685
0	4	180	199
0	6	377	317
0	8	359	-398
1	0	94	76
1	1	443	401
1	2	41	-15
1	3	492	-482
1	5	514	-478
1	6	235	-239
1	7	372	337
1	8	94	-88
2	0	564	-560
2	1	221	-223
2	2	184	-148
2	3	351	356
2	4	356	354
2	5	282	297
2	6	125	-93
2	7	418	421
2	8	233	-235
3	0	682	-674
3	1	411	429
3	2	635	666
3	4	189	171
3	5	436	391
3	6	564	-560
3	7	79	81
3	8	343	361
3	9	88	-93
4	0	185	74
4	1	147	141
4	2	178	-178
4	3	286	-273
4	4	538	-462
4	6	98	-66
4	7	306	-294
4	8	144	166
5	0	186	-186
5	1	927	-869
5	3	208	197
5	4	144	138
5	5	185	236
5	6	415	389
5	7	485	-388
5	8	203	173
6	0	551	545
6	1	323	331
6	2	481	495
6	3	119	127
6	4	62	42
6	5	271	-212
6	6	157	143
6	7	119	-133
7	0	645	591
7	1	93	-129
7	2	351	-329
7	3	408	-387
7	4	100	-124
7	5	175	-190
7	6	164	203
7	7	196	-138
8	0	588	-583
8	2	151	143
8	3	226	237
8	4	134	-155
8	5	131	143
8	6	269	258
8	7	296	388
9	0	164	188
9	1	397	375
9	2	56	-79
9	3	291	299
9	4	94	-75
9	6	72	93
10	0	112	-138
10	1	145	-147
10	2	393	-368
10	3	208	172
10	4	88	-74
10	5	518	-539
10	6	166	-151
11	0	360	-324
11	1	242	259
11	2	107	-72
11	3	246	-248
11	4	289	266
11	5	183	-186
12	0	56	21
12	3	218	-232
12	4	497	468
13	0	208	-190
13	1	171	-216
13	2	346	321
14	0	105	89

H = 9

K	L	FOBS	FCAL
0	1	171	179
0	3	397	339
0	5	846	-851
0	7	33	-3
1	0	85	-74
1	1	60	-37
1	2	130	-136
1	3	85	-60
1	4	157	-126
1	5	73	-73
1	6	321	334
1	7	368	360
2	0	64	71
2	1	284	277
2	2	383	362
2	3	268	248
2	4	558	519
2	5	78	-125
2	6	506	-440
2	7	85	87
3	0	81	-82
3	1	114	-72
3	2	158	-179
3	4	178	-136
3	6	256	-261
3	7	362	391
4	0	492	-488
4	1	355	-357
4	2	341	-298
4	3	212	208
4	4	122	134
4	5	221	250
4	6	165	-123
5	0	79	-58
5	1	592	546
5	2	160	137
5	3	196	161
5	4	205	182
5	5	78	43
6	0	232	248
6	1	71	-87
6	2	279	-258
6	3	670	-635
7	0	326	-306
7	1	543	-530
7	2	451	408
7	3	74	-39
7	4	134	144
7	5	280	282
7	6	93	126
8	0	684	638
8	1	213	225
8	2	479	471
8	4	322	-314
8	5	143	133
9	0	238	177
9	1	324	-299
9	2	299	-284
9	3	76	77
9	4	457	-435
10	0	213	-205
10	1	89	-73
10	2	242	-248
10	3	435	413
11	1	255	217
11	2	162	-141
12	0	292	-285

H = 10

K	L	FOBS	FCAL
0	0	117	116
0	4	271	-369
1	0	156	142
1	1	262	-241
1	2	213	-144
1	3	104	84
1	4	127	163
1	5	242	-209
2	0	99	125
2	2	121	-102
2	3	220	204
2	5	364	-386
3	1	95	-80
3	2	320	-272
3	3	275	251
3	5	92	102
4	1	359	306
4	2	183	-105
4	3	277	286
4	4	125	126
5	0	91	128
5	1	188	175
5	2	473	-464
6	0	405	-393
6	1	103	140
6	2	144	-164
6	3	176	-137
6	4	311	323
7	0	182	153
7	1	353	316
7	2	471	448
7	3	362	-346
8	0	280	271
8	1	338	-331
8	2	156	157
9	0	181	-178
9	1	315	-270

H = 11

K	L	FOBS	FCAL
0	1	200	-193
1	1	214	-175
2	0	284	275
2	1	117	-136
2	2	132	131
3	0	264	267
3	1	218	-200
3	2	63	60
4	0	261	277
4	1	184	-170
5	0	83	60

TABLE B-2

FINAL POSITIONAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS[a] FOR μ-BIS(DIPHENYLPHOSPHINO)METHANE-μ-DIPHENYLACETYLENE-TETRACARBONYLDICOBALT(0)[b]

ATOM NAME	X	Y	Z
Co1	0.29013(12)	0.40511(7)	0.16834(9)
Co2	0.36081(12)	0.33636(7)	0.05663(9)
P1	0.42922(23)	0.37725(14)	0.27022(18)
P2	0.49280(24)	0.28213(14)	0.14186(18)
C12	0.4670(9)	0.2911(4)	0.2562(6)
CA1	0.2091(8)	0.3650(5)	0.0625(7)
CA2	0.2373(8)	0.3199(5)	0.1235(6)
CCOA	0.1893(10)	0.4198(6)	0.2341(8)
OCOA	0.1191(7)	0.4296(4)	0.2776(6)
CCOB	0.3145(9)	0.4857(6)	0.1308(8)
OCOB	0.3230(7)	0.5372(4)	0.1031(7)
CCOC	0.4184(12)	0.3993(7)	-0.0016(9)
OCOC	0.4467(10)	0.4392(6)	-0.0451(8)
CCOD	0.3367(11)	0.2793(7)	-0.0252(8)
OCOD	0.3143(10)	0.2431(6)	-0.0808(7)
C1A1	0.5647(5)	0.4191(4)	0.2817(5)
C1A2	0.6516(6)	0.3967(3)	0.3431(4)
C1A3	0.7564(5)	0.4270(4)	0.3511(5)
C1A4	0.7743(5)	0.4798(4)	0.2976(6)
C1A5	0.6874(7)	0.5022(3)	0.2362(5)
C1A6	0.5826(6)	0.4718(4)	0.2282(4)
C1B1	0.3960(6)	0.3800(4)	0.3820(4)
C1B2	0.3747(6)	0.3241(3)	0.4285(5)
C1B3	0.3412(7)	0.3298(4)	0.5110(5)
C1B4	0.3291(7)	0.3914(5)	0.5469(4)

TABLE B-2 (CONT'D)

C1B5	0.3505(7)	0.4473(3)	0.5004(5)
C1B6	0.3840(6)	0.4416(3)	0.4179(5)
C2A1	0.6420(5)	0.2983(4)	0.1465(5)
C2A2	0.7196(7)	0.2622(3)	0.2020(5)
C2A3	0.8337(6)	0.2770(4)	0.2086(5)
C2A4	0.8702(5)	0.3280(5)	0.1597(6)
C2A5	0.7927(8)	0.3641(4)	0.1042(6)
C2A6	0.6786(7)	0.3493(4)	0.0976(5)
C2B1	0.4844(7)	0.1938(3)	0.1218(5)
C2B2	0.5412(6)	0.1694(4)	0.0559(5)
C2B3	0.5285(7)	0.1041(5)	0.0310(5)
C2B4	0.4589(8)	0.0632(3)	0.0721(6)
C2B5	0.4021(7)	0.0877(4)	0.1380(6)
C2B6	0.4149(7)	0.1530(4)	0.1629(5)
CP11	0.1177(6)	0.3869(4)	-0.0030(4)
CP12	0.1273(6)	0.4446(4)	-0.0492(6)
CP13	0.0407(8)	0.4638(4)	-0.1131(6)
CP14	-0.0554(6)	0.4253(4)	-0.1308(5)
CP15	-0.0649(6)	0.3676(4)	-0.0845(6)
CP16	0.0216(7)	0.3484(3)	-0.0206(5)
CP21	0.1859(6)	0.2604(3)	0.1580(5)
CP22	0.1525(8)	0.2094(4)	0.1006(4)
CP23	0.1080(8)	0.1524(4)	0.1313(6)
CP24	0.0971(7)	0.1462(4)	0.2194(7)
CP25	0.1306(8)	0.1971(5)	0.2768(4)
CP26	0.1750(7)	0.2542(4)	0.2462(5)
H1A2	0.6390	0.3596	0.3808
H1A3	0.8177	0.4112	0.3944
H1A4	0.8482	0.5011	0.3032
H1A5	0.7000	0.5393	0.1985
H1A6	0.5213	0.4876	0.1849

TABLE B-2 (CONT'D)

H1B2	0.3832	0.2806	0.4032
H1B3	0.3261	0.2904	0.5438
H1B4	0.3055	0.3955	0.6051
H1B5	0.3420	0.4908	0.5257
H1B6	0.3990	0.4810	0.3851
H2A2	0.6938	0.2262	0.2365
H2A3	0.8884	0.2515	0.2478
H2A4	0.9507	0.3384	0.1644
H2A5	0.8185	0.4000	0.0697
H2A6	0.6239	0.3748	0.0585
H2B2	0.5903	0.1982	0.0269
H2B3	0.5685	0.0869	-0.0155
H2B4	0.4499	0.0172	0.0545
H2B5	0.3531	0.0588	0.1670
H2B6	0.3748	0.1702	0.2094
HP12	0.1950	0.4717	-0.0368
HP13	0.0474	0.5044	-0.1458
HP14	-0.1164	0.4388	-0.1758
HP15	-0.1326	0.3404	-0.0969
HP16	0.0149	0.3077	0.0120
HP22	0.1602	0.2138	0.0385
HP23	0.0844	0.1165	0.0909
HP24	0.0658	0.1059	0.2411
HP25	0.1228	0.1927	0.3389
HP26	0.1986	0.2901	0.2866
H121	0.5347	0.2818	0.2936
H122	0.4047	0.2643	0.2657

[a] The estimated standard deviations are right justified to the least significant digits of the fractional co-ordinates. The hydrogen atom co-ordinates were calculated using a C-H bond distance of 0.98Å.

[b] See Figure IV-C-1, page 152 in the text for a description of the numbering scheme used.

TABLE B-3

FINAL THERMAL PARAMETERS[a] ($x10^4$) WITH ESTIMATED STANDARD DEVIATIONS[b] FOR μ-BIS(DIPHENYLPHOSPHINO)METHANE-μ-DIPHENYLACETYLENE-TETRACARBONYLDICOBALT(0)[c]

ATOM NAME	B or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co1	61.0(13)	17.8(4)	42.4(8)	3.3(6)	-3.2(8)	0.6(5)
Co2	71.2(15)	25.1(5)	35.6(8)	4.9(6)	-2.9(8)	0.0(5)
P1	60.9(25)	17.4(8)	33.0(14)	2.9(11)	-0.2(16)	-2.3(9)
P2	65.1(26)	19.1(9)	35.3(15)	5.0(12)	1.7(16)	-4.6(9)
C12	82(10)	13(3)	38(6)	12(4)	8(6)	0(3)
CA1	53(9)	22(3)	46(6)	-8(4)	0(6)	5(4)
CA2	66(10)	19(3)	35(6)	2(4)	-10(6)	2(4)
CCOA	82(12)	22(4)	49(7)	-10(5)	8(8)	3(4)
OCOA	101(9)	43(3)	80(6)	12(4)	33(6)	-3(4)
CCOB	55(10)	26(4)	64(8)	8(5)	-12(7)	6(5)
OCOB	113(10)	23(3)	113(7)	5(4)	5(6)	17(4)
CCOC	117(15)	43(5)	52(8)	1(7)	3(9)	14(5)
OCOC	167(13)	72(5)	114(9)	7(6)	22(9)	51(6)

TABLE B-3 (CONT'D)

CCOD	116(14)	39(5)	50(8)	-8(6)	-18(8)	-12(5)
OCOD	218(15)	69(5)	76(7)	4(7)	-19(8)	-37(5)
C1A1	3.81(24)	C2A1	4.05(24)	CP11	3.98(24)	
C1A2	5.20(28)	C2A2	5.22(28)	CP12	6.98(35)	
C1A3	5.75(30)	C2A3	6.38(32)	CP13	7.47(37)	
C1A4	5.93(31)	C2A4	7.10(36)	CP14	6.20(32)	
C1A5	6.90(35)	C2A5	8.27(40)	CP15	6.87(34)	
C1A6	4.61(26)	C2A6	6.62(34)	CP16	5.55(29)	
C1B1	3.45(22)	C2B1	4.09(24)	CP21	4.35(25)	
C1B2	4.92(27)	C2B2	6.47(33)	CP22	6.30(33)	
C1B3	6.90(34)	C2B3	8.39(40)	CP23	8.76(43)	
C1B4	6.61(33)	C2B4	7.15(36)	CP24	7.93(38)	
C1B5	6.49(33)	C2B5	7.41(36)	CP25	7.27(36)	
C1B6	5.36(28)	C2B6	6.21(32)	CP26	5.58(29)	

[a] These are applied in the expression $\exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$.

[b] Estimated standard deviations are right justified to the least significant digits of the thermal parameter ($\times 10^4$).

[c] See Figure IV-C-1, page 152 in the text for a description of the numbering used.

TABLE B-4

EQUATIONS OF PLANES OF THE RIGID PHENYL RINGS IN $Co_2(CO)_4(PhCCPh)(Ph_2PCH_2PPh_2)$[a]

PLANE CONTAINING:						EQUATION
C1A1	C1A2	C1A3	C1A4	C1A5	C1A	$-0.3812X + 0.6294Y + 0.6771Z - 5.9471 = 0$
C1B1	C1B2	C1B3	C1B4	C1B5	C1B6	$0.9108X - 0.0225Y + 0.4122Z - 5.8469 = 0$
C2A1	C2A2	C2A3	C2A4	C2A5	C2A6	$-0.1984X + 0.6380Y + 0.7441Z - 4.0881 = 0$
C2B1	C2B2	C2B3	C2B4	C2B5	C2B6	$0.6911X - 0.2471Y + 0.6792Z - 4.1266 = 0$
CP11	CP12	CP13	CP14	CP15	CP16	$-0.5226X + 0.5056Y + 0.6864Z - 3.2221 = 0$
CP21	CP22	CP23	CP24	CP25	CP26	$0.9039X - 0.3919Y + 0.1714Z - 0.0534 = 0$

[a] These are the normal equations of the orthogonalized planes. The orthogonalized co-ordinates (X_o, Y_o, Z_o) are obtained from the fractional co-ordinates (X_f, Y_f, Z_f) using:

$$X_o = 11.974X_f - 2.0361Z_f$$
$$Y_o = 20.412Y_f$$
$$Z_o = 15.312Z_f$$

APPENDIX C

TABLE C-1: The observed and calculated structure factors for di-μ-bis(diphenylarsino)methane-μ-diphenylacetylene-dicarbonyldicobalt.

TABLE C-2: Final positional parameters with estimated standard deviations for di-μ-bis(diphenylarsino)methane-μ-diphenylacetylene-dicarbonyldicobalt.

TABLE C-3: Final thermal parameters ($\times 10^4$) with estimated standard deviations for di-μ-bis(diphenylarsino)-methane-μ-diphenylacetylene-dicarbonyldicobalt.

TABLE C-4: Equations of planes of the rigid rings in $Co_2(CO)_2\cdot(PhCCPh)(Ph_2AsCH_2AsPh_2)_2$.

TABLE C-1

K	L	FOBS	FCAL
H = 0			
0	2	545	-555
0	3	378	309
0	4	1024	-1009
0	5	159	-200
0	6	1147	1200
0	7	882	-831
0	9	399	382
0	10	362	384
1	-11	588	608
1	-10	366	-375
1	-8	213	-189
1	-6	347	403
1	-5	612	582
1	-4	1385	-1289
1	-3	1583	1461
1	-2	87	48
1	-1	1182	1155
1	2	1065	1154
1	3	481	477
1	4	556	587
1	5	244	-155
1	6	353	328
1	7	1183	-1270
1	8	710	716
1	11	322	-285
2	-11	193	-97
2	-10	260	-267
2	-9	239	302
2	-8	483	-469
2	-7	237	256
2	-6	551	627
2	-4	502	-434
2	-3	2131	2397
2	-2	2654	-2650
2	-1	203	231
2	0	1712	-1983
2	1	1216	1113
2	2	1061	-1195
2	3	743	-776
2	4	548	-536
2	5	361	-384
2	7	1002	1112
2	9	484	-461
2	10	277	-223
2	11	179	-221
2	12	231	286
3	-11	370	-372
3	-10	394	331
3	-8	247	-198
3	-7	615	636
3	-6	572	-590
3	-5	674	-688
3	-4	1424	1416
3	-3	906	-904
3	-2	523	-552
3	-1	249	236
3	0	785	-827
3	1	591	642
3	2	1588	-1601
3	3	156	-181
3	4	645	-698
3	5	561	598
3	6	805	809
3	8	965	-1043
3	9	677	656
3	10	518	-499
3	11	270	304
3	12	290	-250
4	-10	357	420
4	-9	238	-221
4	-6	481	-562
4	-5	691	746
4	-4	223	277
4	-3	2025	-2142
4	-2	691	688
4	0	641	-995
4	1	1008	1128
4	2	632	679
4	3	180	-23
4	4	814	822
4	5	144	-186
4	6	1063	-1132
4	7	441	-380
4	8	521	548
4	9	330	375
4	10	547	-552
4	11	455	404
4	12	413	-416
5	-10	277	267
5	-9	587	-533
5	-7	172	-117
5	-4	144	-206
5	-3	260	264
5	-2	376	398
5	0	129	-130
5	1	387	-363
5	2	163	206
5	4	132	150
5	6	902	-872
5	7	472	481
5	8	541	575
5	9	1050	-1089
5	10	229	272
6	-9	322	-329
6	-8	662	655
6	-7	331	-328
6	-6	327	-316
6	-4	451	498
6	-2	182	182
6	-1	597	-614
6	0	579	607
6	2	163	74
6	3	628	-661
6	4	566	-503
6	5	122	84
6	6	344	226
6	7	269	204
6	8	347	-336
6	9	393	-419
6	10	738	773
7	-9	393	397
7	-8	337	366
7	-7	629	-699
7	-5	695	761
7	-3	547	-558
7	-2	354	345
7	-1	608	-596
7	1	535	576
7	2	292	-257
7	3	933	-910
7	4	1564	1535
7	5	365	359
7	6	523	-585
7	7	255	194
7	9	177	147
7	10	434	447
7	11	275	-295
8	-8	505	-494
8	-5	413	347
8	-4	745	-767
8	-3	532	569
8	-2	235	-259
8	-1	129	-130
8	0	190	224
8	1	346	339
8	2	1246	-1136
8	3	1233	1152
8	4	1129	1125
8	5	1131	-1213
8	6	612	594
8	7	275	299
8	8	347	-298
8	10	280	222
9	11	460	-470
9	-8	204	250
9	-7	243	262
9	-6	543	-528
9	-5	183	143
9	-4	534	-552
9	-3	412	474
9	-1	270	270
9	0	789	-832
9	1	780	815
9	2	437	-447
9	3	936	933
9	4	1084	-1063
9	5	163	163
9	6	574	574
9	7	277	-323
9	8	244	-240
9	9	331	284
9	10	429	-428
10	-7	514	-526
10	-6	393	396
10	-1	872	-939
10	0	706	745
10	1	469	472
10	2	709	-691
10	3	367	365
10	4	559	-615
10	5	474	517
10	6	394	-416
10	8	591	-578
10	9	233	216
10	11	377	328
11	-6	654	671
11	-5	434	-420
11	-4	546	505
11	-3	320	-329
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13	-2	496	-441
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14	2	345	-318
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16	3	206	-155
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-15	-7	343	-310
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-14	-8	205	-220
-14	-6	501	504
-14	-5	285	-249
-14	-2	336	-327
-14	-1	159	148
-13	-6	352	365
-13	-5	292	-303
-13	-3	618	-598
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-13	1	436	-340
-13	2	424	395
-13	3	193	154
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-12	-9	701	716
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-12	-1	345	-902
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-11	2	390	-418
-11	3	417	424
-11	4	722	-732
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-10	-9	245	-98
-10	-8	252	294
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-10	-3	142	130
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-10	0	479	-507
-10	1	239	-249
-10	2	380	-362
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-10	5	875	888
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-9	-10	514	460
-9	-9	377	-415
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-9	-1	575	-560
-9	1	463	-448
-9	2	800	818
-9	3	275	232
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-9	9	309	-244
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-8	-6	739	-762
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-7	3	324	-272
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-7	9	324	-327
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-6	-2	399	341
-6	0	949	-923
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-6	4	987	-811
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-6	9	338	-239
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-5	-10	626	-617
-5	-9	272	-319
-5	-8	1027	1037
-5	-7	523	-511
-5	-6	648	-638
-5	-4	860	-793
-5	-3	502	503
-5	-2	239	203
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-4	-3	351	416
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-4	6	215	-215
-4	7	487	406
-4	8	535	-506
-4	9	298	266
-4	10	287	249
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-3	-8	503	-618
-3	-7	190	-204
-3	-6	861	933
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-3	-1	196	-190
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-2	-9	184	-86
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-2	-5	374	-409
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-1	-7	608	569
-1	-6	138	-157
-1	-5	703	-681
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-1	1	653	-523
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-1	6	998	1035
-1	7	659	-728
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0	4	571	-644
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0	6	134	-19
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K	L	FOBS	FCAL
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1	-8	230	-225
1	-7	204	-157
1	-6	297	242
1	-5	765	-788
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1	-3	1721	1741
1	-2	341	395
1	-1	2066	2173
1	1	461	404
1	2	1286	-1316
1	3	1206	1132
1	4	604	-570
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1	6	1712	-1654
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1	8	340	293
1	10	539	-449
2	-11	401	-371
2	-10	385	365
2	-9	312	-324
2	-8	268	303
2	-7	336	289
2	-6	1777	-1775
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2	-2	344	-314
2	-1	394	-361
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2	3	259	245
2	4	1088	-1124
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2	7	808	815
2	8	872	-825
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2	10	542	-535
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3	-8	300	349
3	-6	661	-667
3	-5	727	774
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K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
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K	L	FOBS	FCAL
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-7	5	422	376
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-7	7	448	481
-7	8	325	-350
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-6	-11	347	328
-6	-10	300	-346
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-6	-8	1148	1206
-6	-7	592	-648
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-3	-9	193	152
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K	L	FOBS	FCAL
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K	L	FOBS	FCAL
0	-6	712	802
0	-5	628	-623
0	-4	142	190
0	-3	923	-976
0	-2	186	283
0	-1	1626	1732
0	0	494	-408
0	1	160	-155
0	2	1201	1115
0	3	1213	-1240
0	4	197	-101
0	5	880	834
0	6	1685	-1812
0	7	582	615
0	8	333	319
1	-8	262	-286
1	-7	487	490
1	-6	282	337
1	-5	1613	-1628
1	-4	679	715
1	-3	787	-721
1	-2	663	690
1	-1	369	-369
1	0	752	-761
1	1	947	-965
1	2	758	818
1	3	381	-370
1	4	898	930
1	5	1143	-1156
1	6	173	-176
1	7	832	805
1	8	322	-354
1	9	213	-263
2	-11	345	389
2	-10	598	-634
2	-7	538	522
2	-6	1204	-1229
2	-5	541	545
2	-4	827	906
2	-3	292	-341
2	-2	465	395
2	-1	1274	-1421
2	0	979	-1086
2	1	659	595
2	2	1162	1259

K	L	FOBS	FCAL
2	3	1332	-1309
2	4	843	866
2	5	500	-626
2	6	1308	1347
2	7	654	-687
2	9	519	-450
2	10	278	324
3	-10	128	13
3	-9	393	441
3	-7	413	-461
3	-6	569	-618
3	-5	1676	1765
3	-4	1338	-1399
3	-3	525	527
3	-2	710	666
3	-1	204	-74
3	0	673	690
3	1	1229	1275
3	2	2019	-2008
3	3	85	29
3	4	1188	1124
3	5	525	487
3	6	248	-248
3	8	187	169
3	9	336	-321
3	10	515	548
3	11	194	-264
4	-9	273	-226
4	-8	171	-62
4	-6	837	851
4	-5	211	-153
4	-4	666	-669
4	-3	610	648
4	-2	814	-784
4	-1	690	715
4	1	452	489
4	2	1226	-1220
4	3	2130	2053
4	4	802	-723
4	5	217	185
4	6	722	-752
4	7	693	738
4	8	696	-773
4	9	729	769
5	-10	500	-491

K	L	FOBS	FCAL
5	-8	534	539
5	-7	489	-500
5	-6	571	593
5	-5	560	-561
5	-3	493	468
5	-2	514	550
5	-1	1172	-1169
5	0	475	-462
5	1	515	-481
5	2	813	831
5	3	519	-454
5	4	556	-557
5	5	392	348
5	6	163	-184
5	7	384	396
5	8	571	-530
5	9	207	252
5	10	352	-426
5	11	331	347
6	-9	730	706
6	-8	259	-337
6	-7	453	-492
6	-6	434	457
6	-5	346	-396
6	-4	246	208
6	-3	378	349
6	-2	596	-553
6	-1	1128	-1177
6	0	1091	1074
6	1	254	-126
6	3	761	-772
6	4	721	669
6	5	640	-641
6	6	886	894
6	7	530	-548
6	8	348	-376
6	10	228	279
7	-8	397	-384
7	-7	332	332
7	-6	219	134
7	-5	400	-458
7	-3	242	-292
7	-2	510	-468
7	-1	952	966
7	0	599	579

K	L	FOBS	FCAL
7	1	889	-731
7	2	351	340
7	3	548	527
7	4	437	-412
7	6	624	624
7	7	1027	-1036
7	8	587	628
7	9	349	385
7	10	279	-274
8	-7	225	153
8	-5	169	-58
8	-4	238	-273
8	-2	625	703
8	0	274	-297
8	1	302	-289
8	2	830	808
8	3	307	343
8	4	626	-616
8	5	361	326
8	6	233	-225
8	7	261	-190
8	8	786	834
8	9	452	-496
8	10	343	-321
9	-8	224	-159
9	-7	353	411
9	-6	368	-301
9	-5	250	-241
9	-3	1003	1012
9	-2	373	-415
9	0	311	317
9	1	282	-264
9	2	256	270
9	3	143	-118
9	4	642	-587
9	5	286	335
9	6	179	148
9	8	114	-7
9	9	351	-288
9	10	242	227
10	-6	384	-377
10	-5	368	378
10	-4	302	340
10	-3	166	-172
10	-2	779	-787

K	L	FOBS	FCAL
10	-1	1688	1870
10	0	658	-623
10	2	161	153
10	3	530	-538
10	4	196	47
10	5	947	946
10	6	645	-616
10	10	283	-23
11	-6	574	558
11	-3	410	-397
11	-2	500	508
11	0	927	-911
11	1	634	631
11	2	342	-290
11	4	692	636
11	6	885	-799
11	7	726	673
12	-6	166	-169
12	-5	444	-431
12	-4	461	449
12	-3	236	-205
12	-2	552	521
12	-1	744	-710
12	0	175	114
12	2	185	109
12	3	228	-203
12	5	689	-623
12	6	595	543
12	8	264	-292
13	-4	189	-88
13	-3	335	-344
13	-2	529	478
13	-1	521	-487
13	0	232	260
13	1	242	169
13	3	762	-715
13	4	188	126
13	6	450	377
13	7	588	-590
13	8	303	275
14	-3	467	454
14	-2	194	-149
14	0	269	246
14	2	654	-622
14	3	464	391

K	L	FOBS	FCAL
14	4	229	238
15	0	297	-228
15	1	233	-179
15	3	823	801
15	4	545	-442

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K	L	FOBS	FCAL
-16	-6	334	225
-16	-5	271	-301
-16	-4	393	-339
-16	-3	820	827
-16	-2	568	-554
-15	-5	371	-362
-15	-4	765	717
-15	-3	265	-281
-15	-2	361	-361
-15	-1	377	405
-14	-9	170	24
-14	-8	501	-520
-14	-6	280	243
-14	-3	613	-595
-14	-2	425	443
-14	0	298	244
-13	-10	522	458
-13	-9	680	-672
-13	-7	719	703
-13	-5	604	-612
-13	-3	205	191
-13	-1	166	-66
-13	0	210	257
-13	1	495	-482
-13	2	375	386
-13	3	198	79
-12	-10	205	215
-12	-9	402	-341
-12	-8	528	567
-12	-6	465	-451
-12	-5	292	264
-12	-4	706	728
-12	-3	215	-107
-12	-2	338	-247
-12	1	257	-213
-12	2	691	645
-12	3	317	-410

K	L	FOBS	FCAL
-12	4	361	-333
-11	-11	523	498
-11	-10	228	-181
-11	-9	394	379
-11	-8	335	-390
-11	-6	168	158
-11	-5	485	525
-11	-4	172	-181
-11	-3	183	-218
-11	-2	269	-272
-11	-1	307	355
-11	3	808	-749
-11	4	621	594
-11	5	249	124
-10	-11	400	443
-10	-9	337	-316
-10	-8	529	-553
-10	-7	1116	1143
-10	-6	446	-436
-10	-4	513	-529
-10	-3	171	-150
-10	-2	290	-318
-10	-1	835	875
-10	0	843	-848
-10	3	387	345
-10	4	237	234
-10	5	599	-565
-10	6	209	-66
-9	-12	591	586
-9	-11	269	-235
-9	-10	268	-302
-9	-9	228	-229
-9	-8	660	689
-9	-6	815	-876
-9	-5	276	304
-9	-3	310	-261
-9	-2	549	570
-9	0	1673	-1726
-9	1	1634	1621
-9	2	349	-360
-9	4	249	-234
-9	7	310	301
-8	-12	189	195
-8	-11	644	-656
-8	-10	527	501

K	L	FOBS	FCAL
-8	-8	444	414
-8	-7	979	-998
-8	-6	455	467
-8	-4	334	374
-8	-3	418	-420
-8	-2	868	791
-8	-1	1622	-1591
-8	0	1208	1273
-8	1	558	589
-8	2	1343	-1374
-8	3	287	259
-8	4	166	232
-8	7	281	269
-7	-12	477	-445
-7	-11	380	-348
-7	-9	447	-463
-7	-8	360	365
-7	-7	149	-200
-7	-6	275	276
-7	-5	229	203
-7	-3	971	-920
-7	-2	659	630
-7	-1	397	-401
-7	0	1103	1110
-7	1	2087	-2068
-7	2	637	651
-7	3	392	416
-7	4	162	172
-7	5	294	-310
-7	7	268	-275
-7	8	255	274
-6	-11	289	267
-6	-10	1018	-951
-6	-9	620	652
-6	-6	522	575
-6	-5	289	233
-6	-4	1654	-1591
-6	-3	1926	1819
-6	-2	771	-744
-6	-1	854	-815
-6	0	141	-126
-6	1	137	71
-6	2	907	875
-6	3	305	-317
-6	4	475	422

K	L	FOBS	FCAL
-6	5	508	-486
-6	6	243	288
-6	8	393	389
-5	-11	222	-187
-5	-9	794	833
-5	-8	399	-401
-5	-5	1052	-992
-5	-4	357	382
-5	-3	1861	1863
-5	-2	2046	-1989
-5	-1	2371	2067
-5	0	717	552
-5	1	544	541
-5	2	602	-528
-5	3	467	521
-5	4	633	-691
-5	5	228	257
-5	6	632	666
-5	7	281	-295
-5	8	462	-437
-4	-10	457	378
-4	-9	198	226
-4	-8	374	-437
-4	-7	329	346
-4	-6	228	254
-4	-5	292	-326
-4	-4	546	529
-4	-3	1090	-1097
-4	-2	777	722
-4	-1	2261	2092
-4	0	455	353
-4	1	383	324
-4	2	470	-404
-4	3	757	671
-4	4	703	-722
-4	5	829	910
-4	6	539	-587
-4	7	399	-405
-4	9	798	776
-3	-12	333	316
-3	-11	398	-332
-3	-10	293	359
-3	-9	468	-431
-3	-8	212	-251
-3	-7	755	751

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
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-3	-5	273	-226	-1	1	250	-213	2	-12	481	408	4	-2	225	-192	6	6	288	329	10	-6	465	506
-3	-4	186	-128	-1	3	1689	-1599	2	-11	455	-464	4	-1	587	521	6	7	901	-896	10	-5	313	235
-3	-3	649	-675	-1	4	725	683	2	-9	195	237	4	0	303	312	6	8	233	162	10	-3	617	-577
-3	-2	2386	2213	-1	5	874	855	2	-8	725	718	4	1	1731	-1692	6	9	447	413	10	-2	479	516
-3	-1	289	-267	-1	6	880	-763	2	-7	784	-745	4	2	2068	1978	7	-9	267	-181	10	0	249	-229
-3	0	677	-638	-1	9	240	-226	2	-6	315	-292	4	3	276	-177	7	-7	281	287	10	1	400	394
-3	1	1589	-1312	-1	10	345	289	2	-5	1212	1243	4	4	145	-66	7	-5	419	421	10	2	413	-367
-3	2	286	-154	0	-12	233	-183	2	-4	1039	-1020	4	6	183	158	7	-3	503	-504	10	3	465	-497
-3	3	198	161	0	-11	439	363	2	-3	730	802	4	7	332	-287	7	-2	168	220	10	4	1077	1005
-3	4	194	188	0	-10	299	-302	2	-2	402	342	4	8	480	494	7	-1	1015	1058	10	6	459	-444
-3	6	437	-516	0	-9	417	424	2	-1	1581	-1604	4	10	501	-490	7	0	429	-393	10	9	210	-179
-3	7	269	328	0	-8	1069	-1118	2	0	573	608	5	-10	390	-349	7	1	542	-500	11	-4	240	-170
-3	8	408	377	0	-7	323	308	2	1	1984	1889	5	-9	741	683	7	2	505	-527	11	-2	662	590
-3	9	312	-321	0	-6	258	210	2	2	1822	-1759	5	-8	425	-405	7	3	807	766	11	-1	505	-517
-2	-11	318	-365	0	-4	240	257	2	3	157	-75	5	-7	169	149	7	4	641	-673	11	0	272	268
-2	-10	429	452	0	-3	1244	-1318	2	4	216	-299	5	-5	723	-728	7	5	1170	1207	11	1	178	-170
-2	-9	1089	-1031	0	-2	755	770	2	5	695	762	5	-4	269	-268	7	6	956	-900	11	2	362	-400
-2	-8	472	492	0	0	299	216	2	7	276	248	5	-3	657	635	7	8	536	535	11	3	418	400
-2	-7	788	795	0	1	646	789	2	8	336	-358	5	-2	206	-216	7	10	458	-435	11	4	523	509
-2	-6	628	-637	0	2	153	-67	3	-11	247	-195	5	0	163	-70	8	-7	292	146	11	5	1041	-992
-2	-5	532	-494	0	3	378	-262	3	-10	617	611	5	1	165	-177	8	-5	392	-451	11	6	696	659
-2	-4	1181	1126	0	4	1455	1453	3	-9	362	-334	5	2	775	742	8	-4	286	-313	11	7	186	144
-2	-3	845	-777	0	5	932	-944	3	-8	375	327	5	3	792	-808	8	-3	690	704	11	8	242	-286
-2	-2	424	-416	0	6	574	-533	3	-7	808	-844	5	4	444	501	8	-2	529	546	12	-5	594	562
-2	-1	293	-203	0	7	561	563	3	-6	1543	1615	5	5	1331	-1242	8	-1	569	-605	12	-4	352	-446
-2	0	2381	-2120	0	9	265	-270	3	-3	191	-198	5	6	931	979	8	0	185	146	12	-2	176	162
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-2	2	617	773	1	-11	537	505	3	-1	598	-617	5	8	277	186	8	2	475	451	12	1	382	236
-2	3	642	-673	1	-10	537	-537	3	0	1022	1148	5	9	454	-468	8	4	308	-309	12	2	189	-197
-2	4	444	-468	1	-9	196	-203	3	1	1067	-947	5	10	325	334	8	6	364	-350	12	4	339	-299
-2	5	175	168	1	-8	626	-678	3	2	232	-301	6	-10	426	395	8	7	615	605	12	5	239	-192
-2	6	569	553	1	-7	993	1057	3	3	1551	1517	6	-9	290	217	8	9	355	-351	12	6	671	624
-2	9	598	-613	1	-6	1854	-1057	3	4	148	-203	6	-8	690	-684	9	-8	516	437	12	7	323	-292
-1	-12	335	-340	1	-5	436	409	3	5	292	285	6	-7	701	743	9	-7	190	-247	13	-4	547	-513
-1	-11	128	131	1	-4	642	-598	3	6	215	-271	6	-6	389	-358	9	-6	302	-359	13	-3	467	466
-1	-9	145	-181	1	-3	735	772	3	7	312	284	6	-4	1198	1208	9	-4	540	516	13	-2	388	-316
-1	-8	866	-912	1	-2	719	-726	3	8	573	-577	6	-3	484	-576	9	-2	664	-655	13	-1	292	-231
-1	-7	616	-618	1	-1	2037	2079	3	9	709	788	6	-2	1448	-1484	9	-1	406	423	13	0	373	377
-1	-6	322	-328	1	0	413	-485	3	10	226	-122	6	-1	1399	1427	9	2	703	742	13	1	545	466
-1	-5	273	358	1	1	116	-25	4	-11	471	430	6	0	443	-373	9	3	865	-902	13	2	1040	-1022
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-1	-3	2273	-2304	1	3	184	-60	4	-9	202	-176	6	2	517	-522	9	5	561	560	13	4	178	-214
-1	-2	288	-168	1	4	458	-474	4	-7	327	-388	6	3	492	455	9	8	240	-259	13	5	286	310
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K	L	FOBS	FCAL
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14	-1	384	355
14	0	242	212
14	1	563	-484
14	3	588	-518
14	4	285	-212
14	6	225	-172
15	1	282	-157
15	2	811	781
15	3	565	-471
15	4	188	111

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K	L	FOBS	FCAL
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-16	-5	525	-642
-16	-4	756	733
-16	-2	283	-224
-15	-8	225	-302
-15	-6	266	-250
-15	-4	348	423
-15	-3	525	-527
-15	-2	382	387
-15	-1	182	-181
-14	-9	487	-482
-14	-8	478	-508
-14	-7	667	652
-14	-6	223	-182
-14	-5	425	252
-14	-4	189	-193
-14	-3	209	-87
-13	-9	589	-674
-13	-8	516	536
-13	-7	505	478
-13	-6	856	-855
-13	-5	264	268
-13	-2	223	~~-128~~
-13	-1	327	324
-13	0	652	-674
-13	1	315	326
-13	2	213	134
-12	-11	212	215
-12	-10	358	-277
-12	-9	382	344
-12	-8	313	338

K	L	FOBS	FCAL
-12	-7	432	-461
-12	-6	225	-278
-12	-5	637	668
-12	-2	163	-56
-12	-1	193	-59
-12	0	298	-271
-12	1	742	726
-12	2	292	136
-12	3	629	-579
-12	4	333	343
-11	-8	183	-219
-11	-6	331	469
-11	-3	395	-379
-11	-2	273	-282
-11	-1	583	574
-11	0	171	120
-11	2	591	-531
-11	4	623	614
-11	5	386	-367
-10	-12	575	527
-10	-10	199	-225
-10	-9	661	-673
-10	-8	791	791
-10	-7	394	-311
-10	-5	425	-413
-10	-4	291	323
-10	-3	744	-734
-10	-2	1874	1125
-10	-1	302	-235
-10	0	1129	-1066
-10	1	343	332
-10	5	335	-354
-9	-12	212	114
-9	-11	289	-268
-9	-10	317	-242
-9	-9	609	585
-9	-8	305	258
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-9	-3	144	201
-9	-2	569	527
-9	-1	1832	-1847
-9	0	1139	1130
-9	1	529	511
-9	2	546	-568

K	L	FOBS	FCAL
-9	5	415	-398
-9	6	464	434
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-8	-11	467	411
-8	-9	222	272
-8	-8	328	-331
-8	-7	217	228
-8	-6	441	-459
-8	-5	889	819
-8	-2	1173	-1112
-8	-1	229	-301
-8	0	1648	1628
-8	1	784	-868
-8	2	289	167
-8	3	296	321
-8	4	234	-239
-8	5	235	206
-8	6	524	527
-8	7	639	-638
-7	-12	299	149
-7	-10	293	-312
-7	-9	219	182
-7	-8	586	-572
-7	-7	460	431
-7	-6	502	529
-7	-5	547	639
-7	-4	1297	-1361
-7	-3	652	670
-7	-2	249	-336
-7	-1	1298	1239
-7	0	739	-723
-7	1	266	239
-7	2	274	-235
-7	3	307	304
-7	5	391	456
-7	6	351	-392
-6	-12	482	401
-6	-11	567	-543
-6	-10	269	208
-6	-8	369	-386
-6	-7	415	460
-6	-6	318	357
-6	-5	1253	-1286
-6	-4	842	826
-6	-3	1367	1331

K	L	FOBS	FCAL
-6	-2	1234	-1117
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-6	0	584	-544
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-6	4	847	-848
-6	7	599	620
-6	8	376	-424
-5	-11	295	-276
-5	-10	619	597
-5	-9	269	-236
-5	-7	208	-174
-5	-6	387	-320
-5	-5	281	-303
-5	-4	2233	2217
-5	-3	2437	-2252
-5	-2	384	232
-5	-1	583	463
-5	0	785	693
-5	2	787	770
-5	3	1278	-1208
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-5	5	745	722
-5	7	243	-187
-5	8	320	-281
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-4	-10	417	455
-4	-8	404	-373
-4	-7	231	164
-4	-6	227	-190
-4	-4	907	897
-4	-3	1438	-1421
-4	-2	1029	956
-4	-1	244	207
-4	0	139	-116
-4	1	704	-653
-4	2	452	365
-4	3	670	-653
-4	4	1268	1251
-4	5	321	-334
-4	6	260	-286
-4	7	288	-312
-4	8	570	590
-4	9	241	-168

K	L	FOBS	FCAL
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-3	-10	378	387
-3	-9	638	-594
-3	-7	431	427
-3	-6	664	-699
-3	-5	169	-163
-3	-3	898	919
-3	-2	1504	-1186
-3	-1	152	-42
-3	0	523	-469
-3	1	595	-556
-3	2	1105	970
-3	4	323	-299
-3	5	697	-670
-3	6	351	347
-3	7	182	45
-3	8	536	621
-3	9	832	-877
-2	-12	327	-254
-2	-11	437	434
-2	-10	610	-605
-2	-9	230	-124
-2	-8	949	883
-2	-7	181	-123
-2	-6	1170	-1154
-2	-5	541	548
-2	-4	561	468
-2	-3	396	358
-2	-2	1269	-1208
-2	-1	669	-630
-2	0	616	-541
-2	1	799	832
-2	2	387	388
-2	3	747	-687
-2	4	891	-877
-2	5	981	997
-2	6	296	-274
-2	7	239	186
-2	8	260	-202
-2	9	393	-471
-1	-12	234	-235
-1	-11	237	183
-1	-10	414	-332
-1	-9	752	766

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-1	-6	580	503
-1	-5	685	668
-1	-3	653	587
-1	-2	685	-615
-1	-1	471	-542
-1	0	271	-219
-1	1	937	920
-1	2	1267	-1077
-1	3	149	-158
-1	4	1250	1228
-1	5	186	-234
-1	6	752	-831
-1	7	716	739
-1	8	664	-668
-1	9	271	304
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0	-11	206	154
0	-10	260	241
0	-9	390	-354
0	-8	417	-320
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0	-5	355	266
0	-4	558	-504
0	-3	572	559
0	0	138	181
0	1	402	-359
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0	9	507	570
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1	-11	384	-323
1	-9	273	-291
1	-8	1112	1026
1	-7	638	-708
1	-6	130	106
1	-4	638	-661
1	-3	209	230
1	-2	1100	1278
1	-1	1533	-1562
1	0	319	-197
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K	L	FOBS	FCAL
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1	4	457	-324
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1	7	168	-131
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2	-12	211	-183
2	-11	558	-571
2	-10	279	288
2	-9	226	244
2	-8	211	117
2	-7	871	-832
2	-6	604	863
2	-5	734	-781
2	-4	583	468
2	-2	183	-218
2	-1	1681	-1797
2	0	2713	2751
2	1	793	-767
2	2	372	-336
2	3	922	954
2	4	145	-58
2	5	152	-123
2	6	444	461
2	7	356	-346
2	8	454	-412
2	9	278	-295
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3	-11	522	470
3	-9	251	284
3	-8	526	-454
3	-7	173	210
3	-6	188	-197
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4	-9	501	452
4	-8	613	-509
4	-7	738	764
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4	-3	1103	1166
4	-2	406	-423
4	-1	1333	1334
4	0	966	-951
4	1	465	425
4	3	157	97
4	5	412	-401
4	6	225	-202
4	7	384	372
4	8	388	402
4	9	508	-563
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5	-7	660	599
5	-6	262	-333
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5	-1	304	293
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5	2	356	-439
5	3	193	50
5	4	929	-928
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5	7	873	357
5	8	620	-591
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6	-8	378	399
6	-6	237	-128
6	-5	428	427
6	-4	828	854
6	-3	1569	-1564
6	-2	424	462
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6	0	254	-325
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6	2	325	141

K	L	FOBS	FCAL
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6	6	804	-802
6	8	192	173
6	9	176	136
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7	-3	198	-179
7	-2	991	1050
7	-1	527	-638
7	0	462	411
7	1	416	-398
7	2	271	283
7	3	364	-348
7	4	570	610
7	5	619	-563
7	6	219	-197
7	7	276	269
7	8	554	558
7	9	499	-560
8	-9	267	-301
8	-8	410	303
8	-6	419	-424
8	-3	192	113
8	-1	264	-290
8	2	645	672
8	3	331	-395
8	4	238	-203
8	5	483	-512
8	6	326	371
8	7	219	154
8	9	497	-488
9	-7	654	-650
9	-5	614	547
9	-1	150	-87
9	0	247	-304
9	1	786	786
9	2	441	-429
9	3	610	-646
9	4	198	201
9	5	326	236
9	6	172	-188
9	7	234	193
9	8	390	-373
10	-5	263	221
10	-4	398	-341

K	L	FOBS	FCAL
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10	0	321	280
10	1	156	128
10	2	1033	-995
10	3	746	663
10	4	687	658
10	5	769	-791
10	7	362	326
10	8	483	-461
11	-6	214	-157
11	-4	229	-129
11	0	286	-325
11	1	149	-11
11	2	226	255
11	3	715	731
11	4	451	-360
11	5	302	-237
11	6	492	469
12	-4	192	-38
12	-3	312	349
12	-1	514	-489
12	1	289	301
12	2	176	-135
12	3	343	332
12	4	448	-387
12	5	341	295
13	-4	460	441
13	-2	350	-322
13	-1	172	68
13	0	797	701
13	1	877	-762
13	2	270	252
14	-1	423	363
14	0	212	-197
14	1	494	-498
14	2	899	839
14	3	536	-469

H = 5

K	L	FOBS	FCAL
-16	-6	526	-596
-16	-5	304	349
-16	-4	235	270
-16	-3	262	-231
-15	-8	256	-313

K	L	FOBS	FCAL
-15	-7	237	230
-15	-6	300	-293
-15	-5	513	513
-15	-4	323	-244
-15	0	267	-311
-14	-9	958	-999
-14	-8	444	498
-14	-6	217	-241
-14	-3	283	-301
-14	-2	237	273
-14	0	590	-567
-13	-10	420	-468
-13	-8	784	832
-13	-7	492	-489
-13	-4	222	-271
-13	-2	673	634
-13	-1	700	-712
-13	0	196	112
-13	2	330	381
-12	-10	192	-265
-12	-9	341	341
-12	-7	468	-522
-12	-6	358	358
-12	-3	352	358
-12	-2	345	-271
-12	-1	490	-419
-12	0	554	621
-12	1	255	-190
-12	2	233	-90
-11	-6	410	435
-11	-4	213	-103
-11	-3	430	-470
-11	-2	211	197
-11	-1	452	407
-11	0	226	-234
-11	1	201	-159
-11	2	171	-56
-11	3	250	295
-10	-12	402	372
-10	-10	514	-508
-10	-9	718	704
-10	-8	252	-393
-10	-7	1095	245
-10	-6	374	323
-10	-5	585	-541

K	L	FOBS	FCAL
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-10	-3	698	726
-10	-2	479	472
-10	-1	780	-800
-10	0	198	58
-10	1	479	458
-10	2	425	-425
-10	3	357	384
-10	4	271	-49
-10	5	330	-365
-9	-12	238	-247
-9	-10	257	255
-9	-9	546	536
-9	-8	503	-524
-9	-7	548	602
-9	-6	880	-853
-9	-5	377	375
-9	-3	753	800
-9	-2	680	-738
-9	-1	151	-161
-9	0	787	785
-9	2	222	-100
-9	3	463	495
-9	4	808	-789
-9	5	211	223
-9	6	341	394
-8	-12	230	219
-8	-10	641	672
-8	-9	246	-292
-8	-7	371	-470
-8	-6	268	218
-8	-5	765	722
-8	-4	138	-244
-8	-3	339	-245
-8	-2	259	-298
-8	-1	1160	1145
-8	0	143	-134
-8	2	284	-246
-8	5	468	468
-8	6	442	-488
-7	-12	294	408
-7	-11	566	-539
-7	-10	432	414
-7	-9	357	-406
-7	-7	117	16

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-7	-2	463	284
-7	-1	188	223
-7	0	698	-481
-7	1	871	-888
-7	2	519	525
-7	4	295	221
-7	6	444	-465
-7	7	561	579
-6	-13	334	386
-6	-12	440	-457
-6	-11	172	97
-6	-10	251	-154
-6	-9	211	-228
-6	-8	359	145
-6	-7	764	803
-6	-6	707	-646
-6	-5	822	-874
-6	-4	1861	1912
-6	-3	1053	-996
-6	-2	351	221
-6	-1	522	-474
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-6	1	765	-711
-6	2	1738	1645
-6	3	954	-1027
-6	4	156	102
-6	5	214	-181
-6	6	408	401
-5	-13	221	214
-5	-12	194	-218
-5	-9	458	437
-5	-8	332	-360
-5	-7	228	240
-5	-6	1048	-1010
-5	-5	863	984
-5	-3	529	-524
-5	-2	413	466
-5	-1	262	163
-5	0	219	-301
-5	1	865	813
-5	2	348	-274

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-5	4	945	957
-5	6	162	-77
-5	7	358	-432
-5	8	408	472
-4	-12	332	-244
-4	-11	266	297
-4	-10	516	496
-4	-9	416	-377
-4	-6	502	-513
-4	-5	677	698
-4	-4	1650	-1681
-4	-3	1368	1249
-4	-1	1111	1064
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-4	1	374	348
-4	2	1043	-928
-4	3	1007	925
-4	5	216	-158
-4	6	577	-667
-4	7	295	312
-4	8	291	284
-3	-13	244	-258
-3	-11	614	547
-3	-10	415	-361
-3	-9	925	-836
-3	-8	1082	1109
-3	-7	333	-323
-3	-5	342	270
-3	-4	763	-789
-3	-3	398	305
-3	-2	296	221
-3	-1	474	-404
-3	0	705	-755
-3	1	628	574
-3	2	301	337
-3	3	359	349
-3	4	895	-941
-3	5	425	437
-3	6	383	-381
-3	7	590	553
-2	-10	576	-575
-2	-9	609	583
-2	-8	563	552
-2	-7	1214	-1288

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-2	1	638	598
-2	2	866	-777
-2	3	718	-641
-2	4	1095	1064
-2	5	230	155
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-2	7	278	273
-2	8	716	-752
-1	-10	324	271
-1	-9	302	298
-1	-8	479	-524
-1	-6	778	816
-1	-5	416	-402
-1	-4	487	518
-1	-2	237	-186
-1	0	561	720
-1	1	744	-677
-1	2	390	-357
-1	3	638	593
-1	4	570	515
-1	5	761	-758
-1	6	755	759
-1	7	587	-669
-1	9	543	599
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0	-10	169	-127
0	-9	176	-211
0	-7	334	320
0	-6	243	259
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0	-4	326	-368
0	-3	1018	-1018
0	-2	1049	1106
0	-1	166	-93
0	0	480	404
0	1	338	-271
0	3	728	710
0	4	424	-425
0	5	514	-471
0	6	373	395
0	7	464	-568

K	L	FOBS	FCAL
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1	-9	377	446
1	-8	249	-219
1	-7	146	168
1	-5	681	-778
1	-4	199	-290
1	-3	1092	1073
1	-2	145	62
1	-1	1427	-1629
1	0	676	630
1	2	416	-344
1	3	788	806
1	4	787	-795
1	6	239	260
2	-12	576	-515
2	-11	335	308
2	-8	335	-283
2	-7	312	307
2	-6	782	-808
2	-5	802	769
2	-3	452	423
2	-2	1761	-1813
2	-1	1124	1169
2	0	734	775
2	1	1155	[illegible]
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[illegible]	[illegible]	[illegible]	-777
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3	-6	271	254
3	-5	285	254
3	-4	825	-801
3	-1	1754	1887
3	0	870	-861
3	1	300	309
3	2	112	-12
3	3	193	-177

K	L	FOBS	FCAL
3	4	475	464
3	5	479	492
3	6	1804	-1864
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3	8	395	414
4	-11	283	-161
4	-10	394	441
4	-9	580	-609
4	-8	245	252
4	-7	310	280
4	-6	216	230
4	-5	1276	-1312
4	-4	1031	1167
4	-3	141	110
4	-2	293	318
4	0	643	-718
4	1	292	404
4	2	601	521
4	5	168	-166
4	6	168	-204
4	7	631	753
4	8	413	-463
5	-9	231	-257
5	-8	459	523
5	-6	742	-823
5	-5	247	314
5	-4	1314	1540
5	-3	1485	-1716
5	-2	1098	1216
5	-1	828	-895
5	0	252	222
5	2	215	225
5	3	1071	-1109
5	4	425	401
5	6	458	478
5	7	467	-542
6	-9	275	295
6	-6	265	-234
6	-5	782	939
6	-4	731	-893
6	-2	325	337
6	-1	592	-689
6	0	375	363
6	2	576	-550
6	3	395	-422

K	L	FOBS	FCAL
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6	5	496	-548
6	7	276	-381
6	8	356	483
6	9	364	-488
7	-9	209	-190
7	-7	238	258
7	-6	173	-271
7	-5	333	364
7	-4	736	-798
7	-3	604	746
7	-2	439	-443
7	0	421	-465
7	2	351	-356
7	3	960	945
7	4	275	-229
7	5	394	-379
7	7	233	303
8	-8	324	292
8	-7	426	-473
8	-5	169	-95
8	-3	249	182
8	0	549	-565
8	1	729	739
8	3	217	-248
8	4	393	-409
8	5	264	231
8	7	482	546
8	8	654	-691
9	-8	309	-309
9	-7	278	-291
9	-6	374	363
9	-5	310	-356
9	-3	166	123
9	-1	182	-96
9	0	617	606
9	1	173	67
9	2	862	-939
9	4	623	706
9	5	340	-367
9	8	545	-606
10	-7	283	344
10	-6	198	156
10	-5	227	-225
10	-4	198	233

K	L	FOBS	FCAL
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10	0	294	277
10	1	723	-708
10	2	255	162
10	3	789	822
10	5	396	-401
10	6	448	472
10	7	604	-527
11	-6	204	204
11	-5	234	-179
11	-3	218	176
11	-2	340	263
11	-1	400	-417
11	2	381	327
11	4	197	-198
11	5	262	262
11	7	217	-208
12	-5	329	-308
12	-4	219	195
12	-3	455	422
12	-2	613	-603
12	0	785	687
12	1	329	-336
12	2	241	254
12	4	280	-264
12	5	317	298
13	-3	195	-174
13	-2	358	-292
13	-1	777	729
13	0	304	-292
13	2	387	397
13	3	443	-464
14	0	656	-571
14	1	595	541
14	2	311	-307
	H =	6	
-15	-8	388	406
-15	-7	239	-237
-15	-6	248	188
-15	-3	651	-714
-15	-2	496	560
-14	-8	337	316
-14	-7	367	-388

K	L	FOBS	FCAL
-14	-5	227	194
-14	-4	610	-658
-14	-2	547	641
-14	-1	650	-648
-13	-10	568	-625
-13	-9	649	684
-13	-8	182	-158
-13	-4	429	-482
-13	-3	949	970
-13	-2	612	-613
-13	-1	354	-386
-13	0	602	522
-12	-9	442	479
-12	-8	364	-323
-12	-7	213	-179
-12	-5	289	305
-12	-4	244	253
-12	-2	686	-764
-12	-1	748	783
-12	0	170	-164
-12	1	309	295
-12	2	439	-385
-12	3	205	173
-11	-11	290	-233
-11	-10	41	-1
-11	-8	316	-327
-11	-6	680	619
-11	-4	457	-455
-11	-2	347	308
-11	0	167	-125
-11	2	238	-185
-11	3	384	412
-11	4	233	-202
-10	-12	271	229
-10	-11	432	-432
-10	-10	273	360
-10	-9	185	-58
-10	-8	239	-207
-10	-7	443	411
-10	-5	420	-498
-10	-4	331	335
-10	-3	504	448
-10	-2	227	-192
-10	-1	356	-337
-10	0	504	513

K	L	FOBS	FCAL
-10	1	439	-371
-10	2	312	369
-10	3	379	337
-10	4	577	-613
-9	-10	434	406
-9	-9	354	-351
-9	-8	729	756
-9	-7	471	-499
-9	-6	323	-319
-9	-5	175	134
-9	-4	341	417
-9	-2	367	-384
-9	-1	796	738
-9	0	205	181
-9	1	292	-250
-9	2	683	653
-9	3	700	-718
-9	4	214	-224
-9	5	602	592
-8	-10	295	300
-8	-8	146	-106
-8	-7	479	-494
-8	-6	773	860
-8	-5	176	-294
-8	-4	203	200
-8	-3	482	-435
-8	-2	445	431
-8	-1	312	362
-8	1	568	-528
-8	3	265	-272
-8	4	675	636
-8	6	484	-510
-7	-13	339	307
-7	-12	577	-607
-7	-11	657	652
-7	-10	554	-584
-7	-8	241	-257
-7	-7	1065	1185
-7	-6	617	-596
-7	-5	214	-272
-7	-4	440	492
-7	-3	547	-511
-7	-2	254	258
-7	0	959	-594
-7	1	304	-267

K	L	FOBS	FCAL
-7	2	546	545
-7	3	157	-154
-7	5	385	-436
-6	-10	636	-608
-6	-9	313	301
-6	-8	306	325
-6	-7	165	216
-6	-6	1658	-1694
-6	-5	1484	1461
-6	-4	371	-405
-6	-2	244	138
-6	-1	553	-524
-6	0	1591	-1526
-6	1	1373	1439
-6	2	492	-507
-6	3	505	-506
-6	5	297	314
-5	-13	195	-166
-5	-12	243	66
-5	-11	650	-572
-5	-10	869	904
-5	-9	402	-398
-5	-8	289	271
-5	-7	566	-584
-5	-5	626	686
-5	-4	818	-802
-5	-3	159	145
-5	-2	407	-342
-5	0	589	553
-5	1	1037	946
-5	2	1573	-1567
-5	3	879	919
-5	4	159	-141
-5	6	308	-320
-4	-13	301	-201
-4	-11	434	324
-4	-10	177	93
-4	-9	954	-941
-4	-8	921	883
-4	-7	739	-742
-4	-6	771	790
-4	-5	516	-574
-4	-4	124	-72
-4	-3	380	-329
-4	-2	1341	1219

K	L	FOBS	FCAL
-4	-1	100	-18
-4	0	483	531
-4	1	688	-642
-4	2	528	495
-4	3	565	556
-4	4	445	-418
-4	6	268	-163
-3	-13	168	208
-3	-12	231	144
-3	-11	237	203
-3	-10	1091	-1031
-3	-9	509	480
-3	-8	158	116
-3	-7	528	-502
-3	-6	671	738
-3	-5	589	-606
-3	-3	469	482
-3	-2	873	862
-3	-1	1167	-1209
-3	0	708	653
-3	1	559	-517
-3	2	1030	961
-3	3	821	-809
-3	4	541	501
-3	5	606	-540
-3	6	625	595
-3	8	227	-180
-2	-11	357	-339
-2	-10	226	-105
-2	-9	1055	1091
-2	-8	848	-840
-2	-7	506	560
-2	-6	231	253
-2	-5	511	-515
-2	-3	783	736
-2	-2	1072	-1125
-2	-1	306	376
-2	0	792	716
-2	1	331	-355
-2	2	469	-437
-2	4	395	336
-2	5	421	-428
-2	6	970	950
-2	7	487	-527
-2	8	268	-305

K	L	FOBS	FCAL
-1	-8	422	-355
-1	-7	645	600
-1	-5	722	662
-1	-3	847	-830
-1	-2	517	-482
-1	-1	1037	1018
-1	0	405	-434
-1	2	360	-390
-1	3	1063	1009
-1	4	478	-470
-1	5	502	480
-1	7	456	-509
-1	8	307	369
0	-12	338	282
0	-11	307	-275
0	-8	282	-275
0	-7	496	461
0	-6	638	619
0	-5	714	-722
0	-4	813	-781
0	-3	643	587
0	-2	187	238
0	-1	307	-263
0	1	223	-165
0	3	684	676
0	4	968	-950
0	5	240	140
0	6	239	-142
0	7	308	340
0	8	215	45
1	-12	297	-258
1	-10	394	345
1	-9	223	-271
1	-7	374	-358
1	-6	926	-980
1	-5	568	-491
1	-4	753	689
1	-3	667	662
1	-2	1062	-1058
1	-1	257	283
1	0	774	807
1	1	617	-600
1	2	435	378
1	3	576	-496
1	4	1037	-932

K	L	FOBS	FCAL
1	5	665	701
1	7	268	-202
2	-8	281	297
2	-7	464	-385
2	-6	202	296
2	-5	358	-371
2	-3	985	-913
2	-1	633	611
2	0	468	-574
2	1	527	459
2	2	619	612
2	3	1276	-1224
2	4	528	496
2	5	341	368
2	6	572	-535
2	8	362	358
3	-10	270	295
3	-9	318	-248
3	-8	252	-226
3	-7	176	182
3	-6	818	776
3	-5	702	-713
3	-4	258	192
3	-3	126	-74
3	-2	950	956
3	-1	262	-241
3	1	290	-253
3	4	949	970
3	5	728	-721
3	7	545	543
4	-11	365	314
4	-10	404	-394
4	-8	337	296
4	-7	350	245
4	-6	981	-1033
4	-4	354	292
4	-3	352	-338
4	-2	1030	1132
4	-1	648	-661
4	0	668	-681
4	1	545	587
4	2	560	597
4	3	526	-501
4	5	584	-566
4	6	674	631

K	L	FOBS	FCAL
4	8	182	-94
5	-9	415	359
5	-7	237	-262
5	-6	684	-627
5	-5	1217	1256
5	-4	1039	-1086
5	-3	137	164
5	-1	378	-418
5	1	1116	1115
5	2	876	-831
5	3	234	-228
5	4	238	318
5	6	103	-16
6	-9	365	-302
6	-7	271	-220
6	-6	530	621
6	-5	409	435
6	-4	911	-918
6	-3	693	716
6	-2	854	-922
6	-1	443	445
6	2	1096	-1182
6	3	1585	1412
6	4	301	-223
6	5	201	148
6	6	371	-352
6	8	277	-246
7	-9	224	-259
7	-8	596	576
7	-7	488	-408
7	-6	606	613
7	-5	628	-592
7	-3	181	112
7	-2	517	555
7	0	153	-216
7	1	423	-436
7	2	403	370
7	3	311	301
7	4	469	-469
7	5	190	130
7	7	347	334
7	8	268	-241
8	-8	213	-253
8	-7	174	-164
8	-6	635	564

K	L	FOBS	FCAL
8	-5	765	-783
8	-4	511	538
8	-2	161	71
8	-1	757	-804
8	0	769	768
8	2	225	262
8	3	715	-672
8	4	391	472
8	5	537	-486
8	6	581	456
9	-8	550	-526
9	-7	570	513
9	-4	193	135
9	-2	413	-356
9	-1	311	429
9	0	419	410
9	1	514	-520
9	2	216	-169
9	3	321	255
9	5	226	-202
9	6	543	547
9	7	868	-810
10	-7	242	221
10	-6	314	-232
10	-5	314	275
10	-4	312	-269
10	-2	454	426
10	-1	257	238
10	0	745	-740
10	3	358	308
10	4	332	-309
10	5	355	313
10	6	281	-280
11	-5	226	-286
11	-3	348	277
11	-2	257	-297
11	0	209	180
11	1	172	85
11	4	502	-441
11	5	430	394
12	-4	241	164
12	-3	276	-224
12	-2	330	-320
12	-1	449	464
12	2	391	312

K	L	FOBS	FCAL
12	3	421	-427
13	0	321	-261
13	1	186	236
13	2	195	-193

H = 7

K	L	FOBS	FCAL
-15	-7	205	125
-15	-5	567	593
-15	-4	777	-799
-14	-9	430	373
-14	-8	257	-183
-14	-5	183	-166
-14	-4	704	-706
-14	-3	1300	1269
-14	-2	704	-700
-13	-10	348	387
-13	-8	222	204
-13	-7	330	-394
-13	-6	252	240
-13	-5	521	-542
-13	-4	731	715
-13	-2	748	-792
-13	-1	389	423
-13	0	142	21
-13	1	189	81
-12	-11	291	-214
-12	-10	428	365
-12	-9	176	49
-12	-8	240	-235
-12	-7	278	-284
-12	-6	607	650
-12	-5	202	-278
-12	-4	431	469
-12	-3	792	-830
-12	-2	367	408
-12	0	317	337
-12	1	436	-391
-11	-11	204	-169
-11	-10	308	273
-11	-8	389	-392
-11	-7	684	725
-11	-5	359	-440
-11	-2	258	261
-11	-1	194	-45

K	L	FOBS	FCAL
-11	1	579	-622
-11	2	387	335
-10	-12	273	-211
-10	-11	239	184
-10	-9	421	-416
-10	-8	442	450
-10	-7	361	425
-10	-6	897	-887
-10	-5	222	271
-10	-4	312	285
-10	-3	147	111
-10	-2	157	-153
-10	-1	335	330
-10	0	327	-323
-10	2	393	423
-10	3	214	-298
-9	-12	221	-279
-9	-11	255	192
-9	-10	333	-290
-9	-9	415	418
-9	-8	168	146
-9	-7	542	-587
-9	-5	477	441
-9	-4	192	-126
-9	-2	230	-140
-9	-1	361	282
-9	1	408	455
-9	2	391	-408
-9	3	434	-425
-9	4	348	319
-8	-12	262	-172
-8	-11	476	548
-8	-8	518	-536
-8	-7	465	471
-8	-6	45	3
-8	-5	179	-234
-8	-3	183	-254
-8	-1	237	338
-8	0	442	-400
-8	2	240	-189
-8	3	389	385
-8	5	252	-259
-7	-12	440	450
-7	-11	234	142
-7	-10	520	-474

K	L	FOBS	FCAL
-7	-9	364	-328
-7	-8	558	519
-7	-6	424	-408
-7	-5	526	529
-7	-4	378	-371
-7	-3	472	-330
-7	-2	287	345
-7	-1	319	-290
-7	0	958	-1061
-7	1	828	856
-7	3	228	-178
-6	-12	300	203
-6	-11	746	-735
-6	-10	372	299
-6	-8	555	581
-6	-7	670	-891
-6	-6	422	495
-6	-5	333	362
-6	-4	463	-442
-6	-2	326	339
-6	-1	1599	-1491
-6	0	1061	1063
-6	1	563	551
-6	2	1106	-1023
-6	3	352	305
-6	6	340	261
-5	-12	370	-342
-5	-11	425	418
-5	-9	392	-369
-5	-7	776	-772
-5	-6	916	654
-5	-5	380	366
-5	-4	384	296
-5	-3	902	-896
-5	-2	332	334
-5	-1	482	-473
-5	0	1637	1545
-5	1	1138	-1139
-5	3	402	352
-4	-13	31	-1
-4	-11	752	674
-4	-10	1115	-1015
-4	-9	699	651
-4	-8	407	-397
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K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
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-4	-5	624	614	-2	6	373	-371	1	0	871	-887	4	0	140	-66	8	-4	352	372	-12	-4	273	-291
-4	-4	1389	-1399	-1	-12	256	222	1	1	208	84	4	1	1128	1082	8	-3	373	388	-12	-1	417	369
-4	-3	788	748	-1	-11	288	-244	1	2	696	648	4	2	690	-694	8	-2	1136	-1183	-12	0	283	-177
-4	-2	298	253	-1	-10	753	726	1	3	1222	-1150	4	3	198	183	8	-1	589	676	-11	-11	263	242
-4	-1	158	89	-1	-9	311	-265	1	4	244	231	4	4	453	-364	8	4	546	-553	-11	-9	612	-626
-4	0	389	379	-1	-8	206	-188	1	5	621	618	4	5	277	167	8	6	448	477	-11	-8	271	276
-4	1	774	-754	-1	-7	210	-195	1	6	455	-363	4	6	328	208	9	-6	279	-211	-11	-7	684	697
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-4	4	276	386	-1	-4	457	462	2	-8	316	-349	5	-7	710	-643	9	-1	723	704	-11	-4	297	-339
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-3	-12	190	135	-1	1	384	-400	2	-5	327	314	5	-2	637	-690	9	2	499	-437	-11	-1	387	365
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-3	-8	776	-778	-1	6	492	-541	2	-2	166	-105	5	1	439	-460	9	5	602	606	-10	-9	174	-113
-3	-7	785	719	-1	7	233	165	2	0	221	-222	5	2	856	-839	9	6	478	-455	-10	-8	895	855
-3	-6	680	-698	0	-12	217	-131	2	1	342	346	5	3	734	664	10	-6	191	221	-10	-7	798	-760
-3	-5	219	-194	0	-11	200	98	2	2	861	-856	5	4	380	-370	10	-2	369	379	-10	-1	584	-563
-3	-4	137	-66	0	-10	263	238	2	4	807	802	5	5	401	285	10	-1	569	-612	-10	0	285	-197
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-3	-2	1823	-1760	0	-7	911	905	2	7	332	359	6	-5	527	-463	11	-1	269	-268	-10	2	208	52
-3	-1	498	537	0	-6	562	-602	3	-11	460	357	6	-4	292	262	11	1	384	-262	-10	3	381	-426
-3	0	259	-284	0	-5	487	-537	3	-7	492	420	6	-3	449	-502	11	2	992	561	-9	-12	281	-205
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-3	3	212	187	0	-2	351	300	3	-4	355	-307	6	0	511	519	12	0	179	-209	-9	-8	199	-160
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-3	6	428	588	0	1	780	-719	3	-1	390	435	6	7	185	-203	H =	8			-9	-5	274	-280
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-2	-11	572	-588	0	3	532	-514	3	3	531	533	7	-8	[illegible]	-242	-14	-8	183	244	-9	-3	331	-282
-2	-10	725	679	0	4	234	-187	3	4	163	-125	7	-7	365	403	-14	-6	315	304	-9	0	559	583
-2	-9	303	-314	0	5	437	-412	3	5	509	-598	7	-6	284	332	-14	-5	986	-1004	-9	2	261	-264
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-2	-7	266	-193	1	-12	442	-313	3	7	197	245	7	-3	332	415	-13	-9	303	312	-8	-11	401	395
-2	-6	1597	1632	1	-11	288	126	4	-10	235	-229	7	-1	373	-351	-13	-6	282	-255	-8	-10	315	-214
-2	-3	1386	-1311	1	-10	348	-304	4	-9	288	92	7	0	201	51	-13	-4	946	925	-8	-9	212	-276
-2	-2	1222	-1188	1	-9	197	236	4	-8	331	231	7	2	1082	1090	-13	-3	961	-972	-8	-8	255	254
-2	-1	1663	1578	1	-8	772	686	4	-7	399	-427	7	3	601	-595	-13	-2	453	425	-8	-7	255	-251
-2	0	978	-912	1	-7	494	-543	4	-6	923	-812	7	4	264	314	-13	-1	243	-132	-8	-5	273	259
-2	1	751	723	1	-6	363	-389	4	-5	629	625	7	5	410	-330	-12	-10	185	166	-8	-4	247	-209
-2	2	364	-398	1	-5	718	708	4	-4	446	-462	7	6	324	287	-12	-8	836	-836	-8	-3	191	-217
-2	3	472	423	1	-3	181	-209	4	-3	337	278	8	-8	519	-481	-12	-7	911	912	-8	-2	725	692
-2	4	522	-523	1	-2	443	-441	4	-2	197	138	8	-7	427	389	-12	-6	431	-410	-8	0	308	-299

K	L	FOBS	FCAL
-8	2	236	182
-8	3	210	-44
-8	4	218	296
-7	-12	447	388
-7	-11	405	-341
-7	-10	346	-377
-7	-9	369	324
-7	-6	164	19
-7	-4	247	-323
-7	-3	293	301
-7	-2	520	514
-7	-1	1270	-1229
-7	1	478	476
-7	2	342	-338
-7	3	273	257
-6	-12	443	-444
-6	-9	392	314
-6	-8	278	-199
-6	-7	425	340
-6	-6	358	-252
-6	-4	520	552
-6	-3	346	325
-6	-2	1035	-1027
-6	-1	368	-248
-6	0	870	887
-6	1	719	-708
-6	2	158	-106
-6	3	410	338
-6	4	269	-327
-6	5	331	299
-5	-11	315	283
-5	-10	284	-246
-5	-9	361	267
-5	-8	255	-232
-5	-7	247	225
-5	-5	482	506
-5	-4	827	-847
-5	-3	370	423
-5	-2	457	-498
-5	-1	1186	1157
-5	0	413	-331
-5	1	529	-569
-5	2	418	406
-5	4	152	-21
-5	5	174	179

K	L	FOBS	FCAL
-4	-12	347	255
-4	-11	518	-429
-4	-10	283	200
-4	-8	406	-400
-4	-7	647	654
-4	-6	175	249
-4	-5	1353	-1412
-4	-4	175	-21
-4	-3	1089	1088
-4	-2	846	-847
-4	-1	790	755
-4	0	935	-600
-4	1	210	186
-4	2	289	190
-4	3	428	414
-4	4	425	-466
-4	6	251	-151
-3	-11	551	-451
-3	-10	468	457
-3	-9	578	-513
-3	-8	421	446
-3	-6	151	-188
-3	-5	1138	-1251
-3	-4	2079	2011
-3	-3	1106	-1080
-3	-2	177	-69
-3	-1	408	365
-3	0	332	-349
-3	1	201	161
-3	2	305	245
-3	3	351	-280
-3	4	473	-469
-3	5	510	503
-2	-12	168	-87
-2	-10	403	368
-2	-7	368	-309
-2	-5	256	245
-2	-4	433	417
-2	-3	1077	-1080
-2	-2	1142	1175
-2	-1	352	-347
-2	0	406	465
-2	1	390	-309
-2	2	266	191
-2	3	807	-773

K	L	FOBS	FCAL
-2	4	774	672
-2	5	223	147
-1	-12	585	-456
-1	-11	528	481
-1	-9	271	-220
-1	-8	267	-232
-1	-7	1132	1108
-1	-6	494	-515
-1	-5	326	398
-1	-4	773	-737
-1	-2	447	483
-1	-1	235	203
-1	0	233	198
-1	1	666	-663
-1	2	462	444
-1	3	187	139
-1	4	358	374
-1	5	581	-587
-1	6	219	210
0	-11	368	312
0	-10	597	-524
0	-8	652	593
0	-6	770	-730
0	-5	496	554
0	-3	569	582
0	-2	564	-493
0	-1	347	350
0	0	1235	-1237
0	1	803	763
0	2	314	205
0	4	555	-506
0	5	482	451
1	-10	259	-135
1	-9	409	326
1	-7	996	-893
1	-6	469	516
1	-3	194	110
1	-2	276	-332
1	1	822	814
1	2	1097	-1052
1	3	138	7
1	5	251	262
1	6	491	-566
2	-8	418	-393
2	-7	182	231

K	L	FOBS	FCAL
2	-6	399	331
2	-5	244	-318
2	-4	241	160
2	-3	628	-725
2	-2	200	219
2	-1	263	-334
2	0	718	698
2	1	616	-621
2	2	468	-451
2	3	708	701
2	4	303	317
2	5	815	-783
2	6	245	229
3	-10	322	-297
3	-6	160	48
3	-4	163	-215
3	-2	713	765
3	-1	645	-652
3	0	298	-269
3	2	292	256
3	5	452	-460
3	6	359	463
4	-9	102	-14
4	-8	173	-219
4	-7	317	-275
4	-6	187	165
4	-5	223	-198
4	-4	160	-114
4	-3	766	811
4	-2	292	-337
4	-1	703	-678
4	0	1006	1083
4	1	330	-279
4	2	407	-390
4	3	355	377
4	4	431	-383
4	5	229	107
4	6	265	256
5	-2	582	-605
5	-1	698	678
5	0	578	501
5	1	1143	-1131
5	2	765	760
5	3	205	-73
5	4	242	-95

K	L	FOBS	FCAL
5	5	437	364
5	6	178	-54
6	-9	357	337
6	-8	340	-260
6	-7	205	251
6	-6	395	371
6	-4	331	-366
6	-3	467	541
6	-2	400	-422
6	-1	507	497
6	0	642	-678
6	1	248	-162
6	2	887	943
6	3	168	-139
6	4	263	220
6	6	365	-408
7	-7	424	415
7	-5	601	-604
7	-4	523	529
7	-3	385	360
7	-2	752	-712
7	-1	653	716
7	0	598	-558
7	1	411	441
7	3	321	360
7	4	492	-517
8	-6	361	-338
8	-4	594	573
8	-3	711	-694
8	-2	317	362
8	0	253	-277
8	1	374	297
8	2	193	-144
8	3	211	-130
8	4	313	-302
8	5	386	420
9	-5	213	254
9	-4	251	-276
9	-3	606	-538
9	-2	678	791
9	-1	517	-521
9	0	619	578
9	1	348	-400
9	3	223	-245
9	4	398	434

K	L	FOBS	FCAL
10	-3	232	238
10	-2	225	229
10	-1	286	-154
10	1	421	-414
10	2	308	221
11	-3	261	157
11	-2	244	-252
11	0	281	-339
11	1	617	801
11	2	247	-238

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K	L	FOBS	FCAL
-14	-6	680	-712
-14	-5	188	143
-13	-9	252	171
-13	-8	428	-482
-13	-7	401	326
-13	-6	466	-507
-13	-5	584	635
-13	-4	282	-304
-13	-3	174	-16
-12	-10	393	481
-12	-9	834	-818
-12	-8	375	341
-12	-7	177	123
-12	-5	241	267
-12	-4	304	-350
-12	-1	293	265
-11	-10	277	-256
-11	-9	467	-458
-11	-8	894	955
-11	-7	744	-731
-11	-6	367	415
-11	-3	298	-330
-11	-2	794	767
-11	-1	954	-1005
-10	-10	335	-313
-10	-9	591	517
-10	-7	553	-606
-10	-6	453	466
-10	-5	344	-386
-10	-4	395	325
-10	-1	665	-638
-10	0	663	706

K	L	FOBS	FCAL
-9	-11	252	267
-9	-9	335	382
-9	-8	614	-679
-9	-7	429	369
-9	-5	532	478
-9	-4	361	-393
-9	-2	303	-385
-9	-1	633	649
-8	-12	602	541
-8	-11	374	-237
-8	-10	258	-188
-8	-9	284	252
-8	-8	333	-361
-8	-7	260	308
-8	-4	688	-696
-8	-3	377	433
-8	-2	364	388
-8	0	443	-458
-8	1	517	568
-8	2	374	-382
-8	3	576	606
-7	-11	438	-439
-7	-10	328	298
-7	-7	474	465
-7	-5	687	-699
-7	-4	583	552
-7	-3	569	537
-7	-2	666	-651
-7	-1	192	-209
-7	0	424	389
-7	1	296	-287
-7	3	372	376
-6	-12	232	-184
-6	-8	281	183
-6	-7	403	-426
-6	-5	177	217
-6	-4	178	192
-6	-3	222	-355
-6	-2	613	-615
-6	-1	599	566
-6	1	496	-497
-6	2	411	495
-6	3	352	-341
-5	-12	280	282
-5	-11	328	327

K	L	FOBS	FCAL
-5	-8	403	-428
-5	-6	1051	1022
-5	-5	862	-877
-5	-1	289	299
-5	1	275	-267
-5	2	242	279
-5	3	177	-228
-5	4	248	239
-4	-9	485	-459
-4	-8	264	266
-4	-7	575	515
-4	-6	376	-424
-4	-5	1072	-1066
-4	-4	1175	1246
-4	-3	597	-528
-4	-2	333	415
-4	-1	197	298
-4	0	575	-489
-4	1	319	-296
-4	2	765	786
-4	3	445	-460
-3	-12	303	-284
-3	-11	196	-7
-3	-9	445	377
-3	-6	937	-955
-3	-5	745	652
-3	-3	454	-470
-3	-2	522	547
-3	-1	423	-428
-3	1	659	642
-3	3	891	-886
-3	4	387	366
-2	-12	282	-293
-2	-11	309	284
-2	-8	337	-319
-2	-7	513	510
-2	-6	447	-433
-2	-5	1198	1262
-2	-4	1042	-1127
-2	-3	239	284
-2	-1	316	247
-2	1	191	169
-2	2	927	-923
-2	3	588	468
-2	4	376	416

K	L	FOBS	FCAL
-1	-11	327	315
-1	-10	179	-22
-1	-9	622	-525
-1	-8	759	725
-1	-7	210	-177
-1	-6	157	-163
-1	-5	221	230
-1	-4	461	-406
-1	-3	528	508
-1	-2	178	207
-1	-1	202	265
-1	0	596	-634
-1	2	208	-95
-1	3	723	687
-1	4	902	-508
-1	5	179	250
0	-10	289	-193
0	-9	240	79
0	-8	632	559
0	-7	1285	-1283
0	-6	739	708
0	-5	428	-455
0	-4	281	271
0	-2	161	223
0	-1	899	-900
0	0	442	436
0	1	414	469
0	2	158	-68
0	3	618	-545
1	-11	218	-129
1	-9	434	357
1	-8	503	-475
1	-6	616	562
1	-5	696	-608
1	-4	512	579
1	-3	542	-537
1	-2	451	-459
1	-1	213	-225
1	0	1061	1045
1	1	616	-644
1	2	171	-139
1	3	253	-330
1	4	679	658
1	5	487	-522
2	-8	461	-377

K	L	FOBS	FCAL
2	-7	499	560
2	-5	187	312
2	-4	303	-258
2	-3	150	-55
2	-2	233	202
2	-1	262	282
2	0	310	-364
2	1	491	-537
2	2	260	283
2	3	231	244
2	5	178	-305
3	-8	199	-103
3	-7	241	318
3	-4	465	-432
3	-3	1017	1020
3	-2	290	-406
3	-1	259	-310
3	0	198	124
3	1	426	463
3	2	322	-279
3	3	466	509
3	4	807	-735
3	5	222	205
4	-10	253	185
4	-7	292	226
4	-6	350	-404
4	-4	328	368
4	-2	789	-766
4	-1	639	656
4	0	211	245
4	1	501	-556
4	2	333	389
4	3	237	98
4	4	758	-760
4	5	732	770
5	-5	178	193
5	-4	153	106
5	-3	373	-388
5	-1	347	377
5	0	386	-339
5	2	295	321
5	3	398	-439
5	4	388	363
6	-7	244	307
6	-5	486	-488

K	L	FOBS	FCAL
6	-4	316	344
6	-3	204	-192
6	-1	305	279
6	0	426	-371
6	2	219	107
7	-6	412	-353
7	-4	571	604
7	-3	623	-667
7	-2	362	283
7	0	206	-163
7	1	281	260
7	2	245	168
7	3	376	-379
8	-5	423	370
8	-1	405	-401
8	0	409	377
8	2	203	-320
8	3	277	-380
9	-4	514	-478
9	-3	469	428
9	-2	190	-156
9	-1	214	212
9	1	236	-172
9	2	370	-322
10	-3	378	407
10	-2	228	-123
10	-1	173	111
10	0	285	-323
10	1	191	250

H = 10

K	L	FOBS	FCAL
-13	-7	337	-352
-13	-6	207	100
-12	-9	185	-89
-12	-8	289	367
-12	-7	463	-466
-12	-6	299	286
-12	-4	256	-266
-12	-2	600	702
-11	-10	583	-607
-11	-9	568	602
-11	-8	216	-259
-11	-6	183	136
-11	-4	430	-402

K	L	FOBS	FCAL
-11	-3	693	787
-11	-2	335	-345
-11	-1	343	-396
-10	-9	403	447
-10	-8	323	-348
-10	-7	176	242
-10	-6	207	-211
-10	-3	328	327
-10	-2	961	-1050
-10	-1	823	659
-9	-11	204	-248
-9	-7	277	-220
-9	-6	485	463
-9	-4	323	-244
-9	-3	159	-88
-9	-2	274	305
-9	-1	404	392
-9	0	320	-314
-9	1	245	244
-8	-11	273	-205
-8	-10	373	374
-8	-9	443	-444
-8	-7	399	396
-8	-6	372	359
-8	-5	1072	-1076
-8	-4	616	594
-8	-3	206	-179
-8	-2	485	490
-8	-1	429	-442
-8	0	422	480
-8	1	422	-431
-8	2	322	337
-7	-8	512	537
-7	-7	181	183
-7	-6	760	-736
-7	-5	200	95
-7	-4	467	477
-7	-3	483	-489
-7	1	420	-466
-7	2	887	942
-6	-10	289	263
-6	-8	428	-441
-6	-7	179	-49
-6	-6	212	239
-6	-5	915	494

K	L	FOBS	FCAL
-6	-4	278	-190
-6	-3	282	-221
-6	-2	153	-135
-6	-1	380	366
-6	0	318	-292
-6	1	461	-478
-5	-11	462	417
-5	-9	482	-423
-5	-7	620	694
-5	-5	295	-281
-5	-3	373	-379
-5	-1	847	849
-5	0	623	-665
-5	2	181	129
-4	-10	323	-370
-4	-9	336	253
-4	-8	220	162
-4	-7	150	167
-4	-6	966	-945
-4	-5	668	606
-4	-2	609	558
-4	-1	371	-353
-4	0	725	-753
-4	1	702	766
-4	2	187	-11
-4	3	224	-313
-3	-11	311	-287
-3	-10	282	278
-3	-7	335	-359
-3	-5	942	878
-3	-4	501	-443
-3	-2	414	-406
-3	-1	618	-612
-3	0	511	507
-3	1	563	504
-3	2	810	-826
-2	-11	216	211
-2	-10	424	354
-2	-9	726	-714
-2	-8	555	522
-2	-7	717	-709
-2	-6	549	570
-2	-5	174	-90
-2	-4	332	-329
-2	0	488	431

K	L	FOBS	FCAL
-2	1	715	-720
-2	2	182	-43
-2	3	485	511
-1	-11	338	259
-1	-10	489	-466
-1	-8	238	264
-1	-7	599	-576
-1	-6	653	635
-1	-5	610	-607
-1	-3	239	265
-1	-2	612	564
-1	-1	783	-854
-1	0	322	233
-1	1	204	-210
-1	2	768	755
-1	3	185	-236
-1	4	245	107
0	-10	225	-219
0	-9	725	549
0	-8	865	-835
0	-7	293	278
0	-6	173	208
0	-5	533	-502
0	-4	348	323
0	-3	569	585
0	-2	791	-806
0	0	557	514
0	3	241	-255
0	4	187	215
1	-10	218	169
1	-8	607	-488
1	-7	592	543
1	-6	303	-333
1	-5	434	493
1	-3	144	-99
1	-2	527	-494
1	-1	1056	-1099
1	0	688	-692
1	2	438	-343
1	3	444	486
2	-10	337	275
2	-7	331	359
2	-6	299	344
2	-4	355	-309
2	-2	325	330

K	L	FOBS	FCAL
2	0	605	-554
2	1	450	434
2	2	396	-298
2	3	747	728
2	4	410	-414
3	-9	352	-268
3	-8	307	295
3	-7	276	217
3	-6	257	-159
3	-5	452	-387
3	-4	613	679
3	-3	270	-263
3	-1	164	-210
3	0	434	424
3	1	395	-421
3	2	529	569
3	3	177	-23
3	4	543	-611
4	-8	362	262
4	-7	463	-420
4	-6	348	-321
4	-5	375	382
4	-3	432	-452
4	-2	274	257
4	0	163	181
4	2	428	427
4	3	1024	-1065
4	4	446	393
5	-8	371	-237
5	-6	203	149
5	-5	206	-29
5	-4	155	-211
5	-3	165	-166
5	-2	293	164
5	-1	363	275
5	0	244	-172
5	2	219	-221
5	3	350	-260
6	-7	425	219
6	-6	265	-219
6	-4	218	143
6	-3	253	-246
6	-2	200	170
6	0	539	-537
6	1	430	461

K	L	FOBS	FCAL
6	2	228	-44
7	-6	329	-258
7	-5	559	491
7	-4	308	-379
7	-2	237	285
7	-1	398	-434
7	1	539	538
7	2	433	-436
8	-5	204	149
8	-4	349	-333
8	-3	372	294
8	-2	274	-254
8	0	300	271
9	-2	170	-21
9	-1	205	260

H = 11

K	L	FOBS	FCAL
-11	-7	182	201
-11	-5	526	-517
-11	-4	589	573
-10	-7	287	-323
-10	-6	296	351
-10	-4	638	652
-10	-3	810	-844
-10	-2	254	267
-9	-10	418	386
-9	-9	238	-168
-9	-8	429	-398
-9	-7	441	420
-9	-5	175	-212
-9	-2	438	478
-9	-1	275	-322
-8	-9	327	-266
-8	-8	279	264
-8	-7	348	369
-8	-6	1006	-1022
-8	-5	402	459
-8	-3	190	269
-7	-11	261	141
-7	-10	347	-278
-7	-9	246	282
-7	-8	342	312
-7	-7	740	-740
-7	-5	667	692

K	L	FOBS	FCAL
-7	-4	377	-369
-7	-3	527	408
-7	-2	435	-484
-7	-1	246	308
-7	0	403	-470
-7	1	682	781
-6	-10	205	175
-6	-7	225	-165
-6	-6	216	125
-6	-3	186	-201
-6	-1	289	349
-6	0	343	-330
-6	1	275	219
-5	-11	220	196
-5	-9	236	-204
-5	-8	372	390
-5	-7	222	141
-5	-6	234	-220
-5	-3	631	-613
-5	-2	825	926
-5	-1	334	-348
-5	0	326	-470
-5	1	347	206
-4	-11	461	-459
-4	-8	216	270
-4	-7	352	-356
-4	-6	217	-185
-4	-5	155	66
-4	-4	183	-179
-4	-3	350	312
-4	-2	405	346
-4	-1	999	-1054
-4	0	417	419
-4	1	245	390
-4	2	372	-439
-3	-10	368	329
-3	-7	411	-379
-3	-5	210	124
-3	-3	209	-213
-3	-2	304	-368
-3	0	702	690
-3	1	459	-491
-3	2	311	-291
-2	-11	340	311
-2	-10	484	-443

K	L	FOBS	FCAL
-2	-9	172	167
-2	-8	169	-177
-2	-6	438	419
-2	-4	589	-621
-2	-3	193	109
-2	-2	194	228
-2	1	401	-457
-2	2	210	314
-1	-10	314	-324
-1	-9	531	451
-1	-8	515	-484
-1	-7	440	385
-1	-5	392	-401
-1	-4	158	-84
-1	-3	938	942
-1	-2	715	-674
-1	-1	158	311
-1	0	263	-194
-1	1	179	122
-1	2	175	158
0	-10	352	248
0	-6	449	-411
0	-4	724	718
0	-3	188	-309
0	-2	638	-602
0	-1	938	921
0	0	567	-598
0	1	410	454
1	-10	427	359
1	-9	289	-175
1	-7	232	-42
1	-6	269	293
1	-4	239	282
1	-3	803	-867
1	-2	622	626
1	3	150	37
2	-9	257	-186
2	-7	396	422
2	-5	372	-341
2	-4	354	475
2	-3	320	-315
2	-2	444	479
2	-1	551	-476
2	0	300	310
2	1	563	-573

K	L	FOBS	FCAL
2	2	813	863
3	-8	296	323
3	-6	646	-590
3	-5	547	564
3	1	229	216
3	2	455	485
4	-7	168	-249
4	-5	424	412
4	-4	358	-374
4	-1	226	228
4	0	366	-389
4	1	570	598
4	2	785	-858
5	-7	262	186
5	-3	199	-99
5	0	261	-328
6	-5	274	173
6	-4	212	-208
6	-3	167	63
6	-2	464	366
6	-1	412	-478
7	-3	442	428
7	-2	319	-323
7	-1	279	-278

H = 12

K	L	FOBS	FCAL
-10	-7	396	389
-10	-5	305	391
-9	-7	505	459
-9	-6	639	-647
-9	-5	484	453
-9	-4	469	-487
-8	-9	428	-398
-8	-8	854	921
-8	-7	716	-742
-8	-6	173	-51
-8	-3	225	229
-8	-2	227	207
-7	-8	364	318
-7	-7	626	-629
-7	-6	475	569
-7	-3	179	-259
-7	-1	309	-347
-6	-10	287	-171
-6	-9	28	-2
-6	-3	427	-539
-6	-2	527	615
-5	-10	393	-310
-5	-9	267	268

K	L	FOBS	FCAL
-5	-8	284	-264
-5	-4	308	-358
-5	-3	274	312
-5	-2	298	307
-5	-1	539	-560
-4	-10	198	197
-4	-8	209	-150
-4	-7	181	208
-4	-6	258	-287
-4	-3	391	394
-4	-2	580	-667
-4	0	298	412
-3	-5	297	275
-3	-3	196	-172
-3	-2	283	-211
-3	-1	337	410
-3	1	341	-395
-2	-8	296	-219
-2	-7	348	312
-2	-6	541	474
-2	-5	659	-659
-2	-3	362	341
-2	-2	172	-244
-2	-1	364	374
-2	1	389	-372

K	L	FOBS	FCAL
-1	-9	293	-330
-1	-8	252	333
-1	-6	294	-316
-1	-5	379	-389
-1	-4	620	775
-1	-3	168	-214
-1	-1	235	266
-1	0	256	-318
0	-7	216	-271
0	-6	201	-281
0	-5	207	285
0	-4	351	368
0	-3	671	-761
0	-2	350	523
0	-1	188	-171
1	-8	249	-290
1	-7	266	276
1	-5	284	281
1	-4	249	-307
1	-2	278	315
2	-8	233	291
2	-7	261	287
2	-6	415	-463
2	-5	367	433
2	-4	328	-380

K	L	FOBS	FCAL
2	-3	194	223
2	-1	212	232
2	0	407	-532
3	-7	403	-450
3	-4	206	-213
3	-3	260	272
3	0	254	-297
4	-6	405	411
4	-5	260	-365
4	-4	221	219
4	-3	218	297
4	-2	168	81
5	-2	421	493

H = 13

K	L	FOBS	FCAL
-7	-7	327	328
-6	-8	309	-367
-6	-6	175	141
-6	-4	476	-635
-6	-3	209	331
-5	-5	350	-421
-5	-4	249	266
-5	-3	293	399
-4	-8	230	267

K	L	FOBS	FCAL
-4	-4	214	345
-4	-3	332	-445
-3	-6	184	274
-2	-8	184	185
-2	-7	322	364
-2	-6	178	-202
-2	-5	252	-187
-2	-4	215	290
-1	-6	473	-580
-1	-5	270	337
-1	-3	237	-217
-1	-2	284	282
0	-5	366	436
0	-4	262	-371
1	-4	252	-361
2	-5	282	-318

TABLE C-2

FINAL POSITIONAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS[a] FOR DI-μ-BIS(DIPHENYLARSINO)METHANE-μ-DIPHENYLACETYLENE-DICARBONYLDICOBALT(0)[b]

ATOM NAME	X	Y	Z
Co1	0.31578(17)	0.27155(15)	0.46306(20)
Co2	0.14594(17)	0.19851(15)	0.38388(20)
As1	0.30253(14)	0.37498(12)	0.30865(17)
As2	0.42387(13)	0.17762(12)	0.47964(16)
As3	0.08522(14)	0.28668(12)	0.21369(16)
As4	0.20748(13)	0.10286(12)	0.33533(16)
C13	0.1956(13)	0.3564(11)	0.1695(14)
C24	0.3502(11)	0.0776(10)	0.4368(13)
CA1	0.1891(13)	0.2602(11)	0.4926(15)
CA2	0.2363(13)	0.1893(13)	0.5361(14)
CCO1	0.4017(12)	0.3201(10)	0.5566(15)
OCO1	0.4556(10)	0.3572(8)	0.6184(12)
CCO2	0.0260(12)	0.1531(10)	0.3909(14)
OCO2	-0.0486(9)	0.1292(8)	0.4039(12)
C1A1	0.4159(8)	0.4193(7)	0.2565(11)
C1A2	0.4955(11)	0.4643(8)	0.3175(9)
C1A3	0.5815(8)	0.4910(7)	0.2891(12)
C1A4	0.5880(9)	0.4728(8)	0.1997(13)
C1A5	0.5086(12)	0.4278(9)	0.1387(10)
C1A6	0.4224(9)	0.4010(7)	0.1671(10)
C1B1	0.2661(9)	0.4800(7)	0.3092(13)
C1B2	0.2528(10)	0.5456(10)	0.2203(9)
C1B3	0.2222(10)	0.6171(8)	0.2220(10)
C1B4	0.2047(10)	0.6230(7)	0.3125(14)
C1B5	0.2180(10)	0.5574(10)	0.4013(10)
C1B6	0.2486(9)	0.4858(8)	0.3997(8)

TABLE C-2 (CONT'D)

C2A1	0.5336(8)	0.1997(9)	0.4190(10)
C2A2	0.5615(11)	0.1421(6)	0.3841(11)
C2A3	0.6462(12)	0.1580(8)	0.3525(11)
C2A4	0.7031(8)	0.2316(10)	0.3558(11)
C2A5	0.6752(10)	0.2892(7)	0.3907(11)
C2A6	0.5905(10)	0.2733(7)	0.4223(10)
C2B1	0.5115(8)	0.1312(8)	0.6311(7)
C2B2	0.4990(8)	0.0512(7)	0.6842(10)
C2B3	0.5644(10)	0.0220(6)	0.7895(10)
C2B4	0.6422(9)	0.0728(9)	0.8417(8)
C2B5	0.6547(8)	0.1529(8)	0.7885(11)
C2B6	0.5893(10)	0.1821(5)	0.6832(11)
C3A1	0.0170(8)	0.2372(7)	0.0905(9)
C3A2	0.0345(8)	0.2653(6)	-0.0068(11)
C3A3	-0.0128(10)	0.2248(8)	-0.0893(8)
C3A4	-0.0952(8)	0.1283(6)	0.0228(12)
C3A5	-0.0777(9)	0.1564(8)	-0.0745(10)
C3A6	-0.0479(9)	0.1688(8)	0.1053(8)
C3B1	-0.0186(10)	0.3647(9)	0.1761(10)
C3B2	0.0062(9)	0.4474(10)	0.1533(12)
C3B3	-0.0663(14)	0.5008(6)	0.1306(13)
C3B4	-0.1636(12)	0.4716(10)	0.1307(12)
C3B5	-0.1885(8)	0.3890(12)	0.1535(12)
C3B6	-0.1160(12)	0.3355(7)	0.1762(12)
C4A1	0.2322(10)	0.1247(8)	0.1995(8)
C4A2	0.3091(8)	0.1812(7)	0.1805(9)
C4A3	0.3237(8)	0.1980(7)	0.0819(12)
C4A4	0.2613(11)	0.1582(8)	0.0023(8)
C4A5	0.1844(9)	0.1017(8)	0.0213(9)
C4A6	0.1698(8)	0.0849(6)	0.1199(11)
C4B1	0.1454(10)	-0.0068(6)	0.3423(10)
C4B2	0.0425(9)	-0.0229(7)	0.3285(10)
C4B3	-0.0019(7)	-0.1010(9)	0.3298(10)

TABLE C-2 (CONT'D)

C4B4	0.0566(11)	-0.1629(6)	0.3450(11)
C4B5	0.1595(10)	-0.1468(7)	0.3587(10)
C4B6	0.2039(7)	-0.0688(8)	0.3574(10)
CP11	0.1431(10)	0.3062(7)	0.5375(11)
CP12	0.1904(7)	0.3177(8)	0.6420(10)
CP13	0.1457(11)	0.3627(9)	0.6799(8)
CP14	0.0536(11)	0.3964(7)	0.6131(13)
CP15	0.0063(8)	0.3849(8)	0.5086(11)
CP16	0.0510(10)	0.3399(8)	0.4707(8)
CP21	0.2601(9)	0,1228(6)	0.6374(8)
CP22	0.2152(7)	0.0450(8)	0.6375(8)
CP23	0.2392(9)	-0.0148(5)	0.7334(11)
CP24	0.3081(9)	0.0032(7)	0.8292(8)
CP25	0.3531(8)	0.0810(8)	0.8291(8)
CP26	0.3291(8)	0.1408(6)	0.7332(11)
H1A2	0.4909	0.4771	0.3806
H1A3	0.6376	0.5227	0.3321
H1A4	0.6487	0.4916	0.1796
H1A5	0.5131	0.4150	0.0756
H1A6	0.3664	0.3693	0.1241
H1B2	0.2651	0.5415	0.1565
H1B3	0.2128	0.6694	0.1594
H1B4	0.1831	0.6734	0.3137
H1B5	0.2057	0.5615	0.4652
H1B6	0.2580	0.4396	0.4623
H2A2	0.5214	0.0903	0.3818
H2A3	0.6659	0.1174	0.3279
H2A4	0.7628	0.2428	0.3336
H2A5	0.7153	0.3411	0.3931
H2A6	0.5708	0.3139	0.4469
H2B2	0.4441	0.0153	0.6475
H2B3	0.5556	-0.0345	0.8270

TABLE C-2 (CONT'D)

H2B4	0.6883	0.0522	0.9159
H2B5	0.7096	0.1887	0.8253
H2B6	0.5981	0.2385	0.6457
H3A2	0.0802	0.3135	-0.0173
H3A3	-0.0005	0.2446	-0.1579
H3A4	-0.1110	0.1279	-0.1326
H3A5	-0.1409	0.0801	0.0333
H3A6	-0.0602	0.1490	0.1740
H3B2	0.0749	0.4680	0.1532
H3B3	-0.0488	0.5591	0.1146
H3B4	-0.2148	0.5093	0.1147
H3B5	-0.2571	0.3684	0.1536
H3B6	-0.1335	0.2772	0.1923
H4A2	0.3531	0.2093	0.2366
H4A3	0.3779	0.2379	0.0685
H4A4	0.2716	0.1701	-0.0672
H4A5	0.1404	0.0736	-0.0348
H4A6	0.1156	0.0450	0.1333
H4B2	0.0012	0.0208	0.3178
H4B3	-0.0745	-0.1123	0.3210
H4B4	0.0253	-0.2180	0.3459
H4B5	0.2008	-0.1905	0.3694
H4B6	0.2765	-0.0574	0.3671
HP12	0.2553	0.2940	0.6891
HP13	0.1790	0.3708	0.7536
HP14	0.0221	0.4282	0.6398
HP15	-0.0586	0.4087	0.4615
HP16	0.0177	0.3318	0.3970
HP22	0.1665	0.0323	0.5699
HP23	0.2075	-0.0696	0.7334
HP24	0.3251	-0.0390	0.8968
HP25	0.4017	0.0937	0.8966
HP26	0.3608	0.1957	0.7332

TABLE C-2 (CONT'D)

H131	0.2230	0.3268	0.1414
H132	0.1697	014054	0.1278
H241	0.3833	0.0627	0.3984
H242	0.3457	0.0406	0.4995
Cl1	0.5712(7)	0.6864(6)	0.1136(7)
CS1	0.4374(21)	0.6635(23)	0.0866(31)
CS2	0.3852(41)	0.7326(20)	0.0720(27)
Cl2	0.3727(10)	0.7871(7)	-0.0665(11)

a The estimated standard deviations are right justified to the least significant digits of the fractional co-ordinates. The hydrogen atom co-ordinates were calculated using a C-H bond distance of 0.98Å.

b See Figure IV-C-4 , page 167 in the text for a description of the numbering scheme used.

TABLE C-3

FINAL THERMAL PARAMETERS[a] ($x10^4$) WITH ESTIMATED STANDARD DEVIATIONS[b] FOR DI-μ-BIS(DIPHENYLARSINO)METHANE-μ-DIPHENYLACETYLENE-DICARBONYLDICOBALT(0)[c]

ATOM NAME	B or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co1	31.6(17)	29.0(13)	62.6(25)	7.5(12)	5.7(17)	-15.6(15)
Co2	36.0(18)	27.5(13)	54.7(24)	7.5(12)	4.6(16)	-14.6(14)
As1	42.9(15)	27.5(10)	63.9(20)	5.0(10)	14.2(14)	-10.5(12)
As2	33.0(14)	29.1(10)	60.9(19)	10.8(9)	3.9(13)	-16.1(11)
As3	43.7(15)	30.5(11)	55.6(20)	13.3(10)	2.3(14)	-10.5(12)
As4	35.3(14)	27.1(10)	55.1(19)	7.6(10)	2.8(13)	-12.9(11)
C13	53(15)	34(10)	63(18)	-1(10)	19(13)	-15(11)
C24	33(12)	45(10)	55(16)	30(9)	-30(11)	-15(10)
CA1	59(15)	22(9)	66(19)	7(9)	28(14)	-23(11)
CA2	53(16)	64(13)	37(17)	19(11)	10(13)	-18(12)
CCO1	62(15)	40(9)	102(20)	12(9)	39(14)	-34(11)
OCO1	88(12)	52(8)	135(17)	-4(8)	16(11)	-46(10)
CCO2	61(14)	31(9)	62(18)	-5(9)	19(13)	-38(11)
OCO2	53(10)	67(9)	159(18)	-12(7)	58(11)	-22(10)

TABLE C-3 (CONT'D)

C1A1	3.75(44)	C2B1	3.45(42)	C4A1	3.10(40)
C1A2	5.21(51)	C2B2	3.50(42)	C4A2	4.66(48
C1A3	5.48(52)	C2B3	4.74(40)	C4A3	4.80(49)
C1A4	7.11(62)	C2B4	5.22(51)	C4A4	5.36(52)
C1A5	7.53(64)	C2B5	5.66(54)	C4A5	6.00(55)
C1A6	5.96(55)	C2B6	5.52(53)	C4A6	4.40(47)
C1B1	4.59(48)	C3A1	3.50(42)	C4B1	3.95(44)
C1B2	5.58(53)	C3A2	4.30(46)	C4B2	4.27(47)
C1B3	6.37(58)	C3A3	5.12(51)	C4B3	6.34(57)
C1B4	7.29(63)	C3A4	4.71(48)	C4B4	5.70(54)
C1B5	6.03(56)	C3A5	5.46(52)	C4B5	5.27(52)
C1B6	5.35(52)	C3A6	4.82(49)	C4B6	4.46(47)
C2A1	3.98(44)	C3B1	3.51(42)	CP11	2.95(40)
C2A2	6.54(59)	C3B2	7.01(62)	CP12	4.92(49)
C2A3	7.58(65)	C3B3	9.52(77)	CP13	6.53(59)
C2A4	6.97(61)	C3B4	8.20(68)	CP14	5.24(52)
C2A5	5.74(54)	C3B5	8.53(72)	CP15	6.23(57)
C2A6	3.85(44)	C3B6	7.11(61)	CP16	5.71(54)
CP21	3.35(42)	CP22	3.20(41)	CP23	3.97(44)
CP24	5.14(50)	CP25	4.60(48)	CP26	3.70(43)

TABLE C-3 (CONT'D)

Cl1	221(11)	119(11)	148(6)	-11(9)	62(6)	-12(8)
CS1	86(26)	180(29)	288(62)	20(23)	96(33)	-18(35)
CS2	711(11)	104(22)	423(42)	93(38)	499(62)	3(24)
Cl2	435(18)	130(9)	362(20)	52(10)	49(15)	18(10)

a These are applied in the expression $\exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$.

b Estimated standard deviations are right justified to the least significant digits of the thermal parameter (x10^4).

c See Figure IV-C-4 , page 167 in the text for a description of the numbering scheme used. B values are quoted for the ring carbon atoms.

TABLE C-4

EQUATIONS OF PLANES OF THE RIGID PHENYL RINGS IN $Co_2(CO)_2(PhCCPh)(Ph_2AsCH_2AsPh_2)_2$ [a]

PLANE CONTAINING:						EQUATION
C1A1	C1A2	C1A3	C1A4	C1A5	C1A6	$+0.2380X - 0.7748Y + 0.5857Z + 2.6642 = 0$
C1B1	C1B2	C1B3	C1B4	C1B5	C1B6	$+0.8737X + 0.2834Y + 0.3954Z - 6.0179 = 0$
C2A1	C2A2	C2A3	C2A4	C2A5	C A6	$+0.2664X - 0.2142Y + 0.9398Z - 5.5130 = 0$
C2B1	C2B2	C2B3	C2B4	C2B5	C2B6	$-0.7928X + 0.4939Y + 0.3570Z - 1.1489 = 0$
C3A1	C3A2	C3A3	C3A4	C3A5	C3A6	$+0.6898X - 0.6242Y + 0.3668Z + 2.4756 = 0$
C3B1	C3B2	C3B3	C3B4	C3B5	C3B6	$-0.0445X + 0.2286Y + 0.9725Z - 3.7699 = 0$
C4A1	C4A2	C4A3	C4A4	C4A5	C4A6	$+0.5410X - 0.7538Y + 0.3731Z - 0.3864 = 0$
C4B1	C4B2	C4B3	C4B4	C4B5	C4B6	$-0.1268X + 0.0775Y + 0.9889Z - 4.1836 = 0$

[a] These are the normal equations of the orthogonalized planes. The orthogonalized co-ordinates (X_o, Y_o, Z_o) are obtained from the fractional co-ordinates (X_f, Y_f, Z_f) using:

$$X_o = 14.001X_f - 4.6544Z_f$$
$$Y_o = 12.413X_f + 17.321Y_f + 3.8718Z_f$$
$$Z_o = 12.330Z_f$$

APPENDIX D

TABLE D-1: The observed and calculated structure factors for xyleneenneacarbonyltetracobalt.

TABLE D-2: Final positional parameters with estimated standard deviations for xyleneenneacarbonyltetracobalt.

TABLE D-3: Final thermal parameters ($x10^4$) with estimated standard deviations for xyleneenneacarbonyltetracobalt.

TABLE D-1

K	L	FOBS	FCAL
H = 0			
1	1	640	-705
1	2	2312	3139
1	3	967	976
1	4	476	475
1	5	279	276
1	6	456	-427
1	7	1082	-1131
1	8	1119	-1157
1	9	314	314
1	10	1055	-1116
1	11	417	426
1	12	599	605
1	13	392	-414
1	14	518	533
1	16	476	495
1	17	284	317
1	18	129	-149
1	20	380	-392
2	0	1246	-1076
2	1	231	-148
2	3	347	-267
2	4	874	-843
2	5	335	365
2	6	1037	980
2	8	1247	1212
2	9	348	-333
2	10	1259	-1272
2	11	555	562
2	12	545	-561
2	14	412	426
2	15	508	-519
2	17	191	232
2	18	415	434
2	19	182	170
3	1	752	-746
3	3	989	846
3	5	467	-406
3	6	925	-928
3	7	402	-395
3	8	1065	1043
3	9	115	120
3	10	323	359
3	12	783	-791
3	13	309	330
3	14	119	145
3	15	346	-357
3	16	166	-197
3	18	297	-323
3	19	146	-186
3	20	265	252
4	0	1362	1322
4	1	711	-696
4	[illegible]	196	-204
4	[illegible]	521	498
4	5	793	765
4	6	134	169
4	7	548	-534
4	8	307	-273
4	10	228	230
4	11	602	612
4	12	147	-169
4	13	181	162
4	16	314	328
4	18	128	-157
4	19	153	137
5	1	636	604
5	2	363	342
5	3	1032	-1021
5	4	802	-772
5	5	233	259
5	6	172	179
5	7	288	-249
5	8	310	249
5	9	431	-440
5	11	316	281
5	17	185	-191
5	19	132	-115
6	0	271	-273
6	1	559	561
6	2	619	613
6	3	652	657
6	4	167	-208
6	6	762	-748
6	7	186	174
6	8	187	-189
6	9	904	-930
6	10	544	536
6	11	305	272
6	13	258	277
6	17	221	178
7	1	508	-504
7	2	325	344
7	3	140	116
7	4	643	659
7	7	875	873
7	8	508	-512
7	9	388	-353
7	10	243	-254
7	11	755	-714
7	14	162	170
8	0	753	-749
8	1	294	-317
8	3	424	-438
8	4	416	404
8	5	323	-309
8	7	184	158
8	9	886	879
8	10	183	-151
8	12	193	-167
8	13	332	-354
9	1	499	524
9	2	482	-529
9	3	280	-294
9	4	146	149
9	5	149	-175
9	7	358	-414
9	11	445	472
10	1	495	507
10	3	198	235
10	6	137	159
H = 1			
0	-20	340	-370
0	-18	290	-310
0	-16	659	680
0	-14	277	330
0	-12	108	-97
0	-10	203	-218
0	-8	1032	-1072
0	-6	717	762
0	-4	277	-302
0	-2	2779	3155
0	2	2966	-3258
0	4	240	181
0	6	1095	-1207
0	8	319	349
0	10	1337	1474
0	12	294	-286
0	14	859	-915
0	16	356	-371
0	18	188	207
0	20	372	331
1	-18	544	-556
1	-15	288	-292
1	-12	266	265
1	-10	948	980
1	-9	517	-536
1	-8	608	-639
1	-7	197	194
1	-6	581	641
1	-5	1056	1005
1	-4	687	-669
1	-3	945	-997
1	-2	162	-148
1	-1	942	-899
1	0	3151	3060
1	1	168	-192
1	3	347	-368
1	4	692	-691
1	6	639	-661
1	7	1024	1032
1	8	978	-1002
1	9	265	251
1	10	598	602
1	11	659	-694
1	12	956	1006
1	15	476	511
1	18	391	-411
1	21	167	148
2	-20	212	266
2	-19	257	-307
2	-17	257	237
2	-16	180	-160
2	-15	361	350
2	-12	678	-693
2	-11	387	406
2	-10	789	838
2	-9	332	-322
2	-8	1384	1332
2	-7	1128	-1085
2	-6	443	-433
2	-5	1587	1485
2	-4	301	250
2	-3	1536	1393
2	-2	594	-597
2	0	668	-638
2	1	345	-298
2	2	721	697
2	3	461	-432
2	4	281	297
2	5	323	305
2	6	443	-432
2	8	630	-647
2	9	1140	1130
2	10	617	-654
2	11	330	294
2	12	736	745
2	13	742	-796
2	15	145	-83
2	16	140	136
2	17	208	217
2	18	154	165
2	20	475	-462
3	-20	149	131
3	-18	262	290
3	-17	422	-453
3	-16	269	-277
3	-14	426	429
3	-13	365	360
3	-12	179	-200
3	-11	391	405
3	-10	1261	-1230
3	-9	626	625
3	-8	1083	1050
3	-7	1006	-931
3	-6	906	895
3	-5	481	-537
3	-4	1538	-1472
3	-2	315	314
3	-1	957	867
3	0	909	-827
3	1	945	824
3	2	996	947
3	3	990	971
3	4	193	-184
3	5	1286	-1201
3	6	776	724
3	7	235	209
3	8	288	273
3	9	196	-221
3	10	718	-689
3	11	541	524
3	13	466	477
3	14	354	369
3	15	282	-276
3	16	384	-378
3	18	368	369
4	-19	305	284
4	-18	242	212
4	-17	222	208
4	-16	306	277
4	-15	514	-504
4	-14	273	-297
4	-13	473	-467
4	-12	218	229
4	-11	196	229
4	-10	525	-511
4	-9	911	931
4	-8	401	-408
4	-7	265	245
4	-6	1431	1346
4	-5	314	-314
4	-4	198	183
4	-3	477	455
4	-1	1145	-1093
4	0	563	-541
4	1	220	-194
4	2	206	-192
4	3	1917	1763
4	4	263	250
4	7	481	-481
4	9	178	197
4	11	406	-366
4	12	613	-607
4	14	173	204
4	15	364	357
4	19	157	-83

K	L	FOBS	FCAL
5	-19	277	-303
5	-18	189	-164
5	-17	282	274
5	-16	155	132
5	-15	193	210
5	-14	521	544
5	-13	226	-216
5	-11	395	-389
5	-10	423	-421
5	-9	338	-325
5	-8	365	-358
5	-7	299	272
5	-6	414	387
5	-5	124	114
5	-4	340	332
5	-3	161	125
5	-1	297	292
5	0	627	597
5	1	1743	-1694
5	2	822	-805
5	3	500	-496
5	4	659	-606
5	5	1163	1126
5	6	488	454
5	7	269	-289
5	9	296	304
5	10	116	-65
5	13	443	-428
5	14	155	-191
5	18	145	122
6	-16	323	-325
6	-15	161	135
6	-14	134	149
6	-12	556	575
6	-11	658	680
6	-8	524	-524
6	-7	835	-885
6	-6	165	-281
6	-5	381	305
6	-4	477	455
6	-2	311	-296
6	-1	714	697
6	0	568	557
6	1	618	623
6	2	295	297

K	L	FOBS	FCAL
6	3	651	-625
6	4	1056	-1041
6	6	195	-174
6	7	213	-243
6	8	616	631
6	10	210	191
6	11	674	655
6	13	249	-227
7	-14	198	-172
7	-13	306	-321
7	-11	270	-268
7	-10	152	189
7	-9	963	979
7	-7	162	170
7	-6	329	-319
7	-5	557	-567
7	-4	360	-372
7	-3	292	282
7	-2	203	-118
7	-1	413	-414
7	0	231	217
7	1	253	224
7	2	543	565
7	3	472	488
7	5	367	369
7	6	540	-558
7	7	133	-74
7	8	181	-169
7	9	730	-730
7	10	191	189
7	11	214	191
7	12	128	136
7	13	287	284
7	14	131	141
8	-11	599	-642
8	-9	181	-238
8	-7	657	660
8	-6	166	211
8	-5	178	173
8	-3	169	186
8	-2	494	-494
8	1	595	-603
8	2	411	410
8	5	246	230
8	7	523	556

K	L	FOBS	FCAL
8	9	163	134
8	10	255	-229
8	11	534	-550
9	-9	447	-477
9	-4	232	262
9	-3	251	293
9	-1	474	503
9	0	521	-573
9	1	292	-309
9	2	144	203
9	3	456	-477
9	4	219	220
9	6	267	-261
9	7	305	-330
9	9	479	525
9	11	175	194
10	-6	143	166
10	-3	413	-432
10	-1	290	-302
10	0	147	-157
10	1	413	427
10	2	235	-253
10	3	320	-346
10	4	209	193
10	5	153	140
10	6	178	142

H = 2

K	L	FOBS	FCAL
0	-20	302	-303
0	-18	456	472
0	-14	422	-437
0	-12	259	259
0	-10	305	-308
0	-8	357	247
0	-4	340	-376
0	-2	603	682
0	0	1159	-1117
0	2	970	1069
0	4	677	-743
0	6	928	-1022
0	8	1291	1371
0	12	1016	-1062
0	16	160	192
1	-16	403	438

K	L	FOBS	FCAL
1	-14	519	-520
1	-12	111	140
1	-11	314	-326
1	-9	384	389
1	-8	446	-452
1	-7	937	948
1	-6	237	232
1	-5	1090	-1033
1	-4	1116	-981
1	-3	847	-727
1	-2	476	456
1	-1	314	358
1	0	329	293
1	1	99	61
1	2	1266	-1258
1	3	125	108
1	4	467	418
1	5	1212	1209
1	6	498	-516
1	7	135	-146
1	8	481	-478
1	9	1025	-1044
1	10	948	1072
1	13	482	514
1	16	149	124
1	17	141	-129
1	19	141	115
1	20	204	210
2	-21	251	-188
2	-18	247	-236
2	-17	342	339
2	-15	122	133
2	-13	130	122
2	-12	193	-160
2	-11	302	-302
2	-10	845	824
2	-9	1178	-1146
2	-8	1011	-997
2	-7	693	663
2	-5	1723	1607
2	-4	1321	-1226
2	-3	1685	-1540
2	-2	1303	-1204
2	-1	402	-371
2	0	350	-386

K	L	FOBS	FCAL
2	1	573	-541
2	2	617	567
2	3	537	-528
2	4	1824	-1782
2	5	379	367
2	6	407	-369
2	7	657	673
2	8	118	-74
2	9	402	408
2	10	678	697
2	11	1066	-1097
2	13	450	-442
2	14	333	-372
2	15	226	265
2	16	178	158
2	18	234	-234
2	19	171	138
2	20	149	-143
3	-19	337	-346
3	-17	259	-308
3	-15	455	462
3	-14	280	293
3	-13	384	433
3	-12	652	-653
3	-11	588	604
3	-10	647	670
3	-9	564	-563
3	-8	878	831
3	-7	1194	-1187
3	-6	1507	-1437
3	-3	1070	1011
3	-2	255	236
3	-1	1346	1265
3	0	725	-710
3	1	335	318
3	2	1313	1225
3	3	869	-823
3	4	641	623
3	5	279	-288
3	6	277	-252
3	7	473	454
3	8	1056	-1003
3	9	409	393
3	11	999	991
3	12	781	790

K	L	FOBS	FCAL
3	13	347	-344
3	14	213	-224
3	15	486	-499
3	16	168	-154
3	19	136	158
4	-20	150	138
4	-19	357	323
4	-17	519	-516
4	-16	221	-224
4	-15	456	-478
4	-14	240	-227
4	-13	426	421
4	-11	596	638
4	-10	591	-595
4	-9	544	530
4	-8	1266	1209
4	-7	213	215
4	-6	395	370
4	-5	690	-701
4	-4	651	-599
4	-3	513	-507
4	-2	535	-479
4	-1	287	-339
4	0	216	-174
4	1	2298	2137
4	2	350	332
4	3	524	509
4	4	896	862
4	5	1460	-1375
4	7	101	-97
4	9	399	-409
4	10	665	-669
4	13	887	865
4	14	337	353
4	17	379	-351
4	19	290	-251
5	-19	254	258
5	-17	410	425
5	-16	461	472
5	-15	417	-419
5	-14	178	-126
5	-13	340	-303
5	-12	527	-524
5	-10	424	-442
5	-9	426	430

K	L	FOBS	FCAL
5	-7	513	485
5	-6	430	402
5	-4	640	647
5	-2	257	281
5	-1	1001	-933
5	0	952	-924
5	1	649	-646
5	2	1197	-1118
5	3	1621	1526
5	4	831	802
5	5	306	309
5	6	395	356
5	7	339	-308
5	8	178	-133
5	10	191	166
5	11	763	-717
5	12	137	-117
5	13	136	154
5	14	171	-188
5	15	403	397
5	16	191	199
5	18	178	288
6	-17	320	349
6	-14	664	701
6	-11	244	158
6	-10	316	-373
6	-9	717	-740
6	-8	275	-283
6	-7	348	353
6	-5	545	555
6	-4	147	-126
6	-3	356	-289
6	-2	342	356
6	-1	289	306
6	0	631	622
6	1	694	-675
6	2	930	-941
6	3	520	-568
6	4	668	-669
6	5	555	529
6	6	571	553
6	7	132	-80
6	9	464	483
6	11	341	-341
6	12	185	216

K	L	FOBS	FCAL
6	13	450	-431
6	14	204	-152
6	16	238	-248
7	-16	157	-156
7	-15	186	181
7	-13	156	-166
7	-11	391	405
7	-10	134	72
7	-9	282	274
7	-8	129	-130
7	-7	441	-456
7	-5	467	488
7	-4	266	-205
7	-3	186	206
7	-2	153	-109
7	-1	209	-198
7	0	402	415
7	1	576	590
7	2	288	240
7	4	195	-163
7	6	235	-232
7	7	174	-159
7	11	380	377
7	12	214	219
7	13	182	-194
7	15	129	102
8	-13	152	-140
8	-11	154	-187
8	-10	159	-139
8	-9	509	552
8	-5	293	-303
8	-4	145	-168
8	-3	366	362
8	-1	369	-375
8	0	274	271
8	2	181	-170
8	3	378	377
8	4	143	145
8	6	220	239
8	9	316	-301
8	10	204	-195
8	12	159	140
9	-5	134	-152
9	-3	264	271
9	-2	282	-300

K	L	FOBS	FCAL
9	0	264	-275
9	1	423	-474
9	2	332	376
9	3	213	224
9	4	354	-360
9	9	342	371
9	10	169	-161
10	-2	279	-314
10	-1	302	352
10	0	245	-272
10	1	333	-329
10	2	169	284
10	4	364	394
10	5	250	232

H = 3

K	L	FOBS	FCAL
0	-16	696	-723
0	-14	776	789
0	-12	477	469
0	-10	486	-456
0	-6	598	-586
0	-4	389	402
0	-2	295	316
0	0	741	752
0	2	2004	2110
0	4	2054	-2056
0	6	359	396
0	8	720	772
0	14	135	78
0	16	451	-435
0	18	233	202
0	20	184	135
1	-18	220	215
1	-16	267	-285
1	-14	513	-513
1	-13	381	-431
1	-12	675	718
1	-9	1132	1151
1	-8	840	830
1	-7	175	-174
1	-6	315	301
1	-5	1174	-1139
1	-4	164	-222
1	-3	930	926

K	L	FOBS	FCAL
1	-2	328	-341
1	-1	271	321
1	0	453	523
1	1	213	236
1	2	525	514
1	3	224	267
1	4	626	654
1	6	1613	-1672
1	7	765	-810
1	8	194	204
1	9	179	-176
1	10	222	219
1	11	177	183
1	12	202	-198
1	14	451	472
1	18	170	-193
1	19	151	-161
2	-19	207	156
2	-17	217	175
2	-16	234	212
2	-14	475	-488
2	-13	250	-247
2	-12	223	224
2	-11	798	-804
2	-10	753	-772
2	-8	430	-422
2	-7	1323	1298
2	-6	1032	1024
2	-5	255	-227
2	-3	796	-809
2	-2	1477	-1490
2	1	1253	-1301
2	2	479	-474
2	3	472	467
2	4	670	645
2	5	828	815
2	6	436	434
2	9	766	-784
2	10	205	210
2	11	496	-487
2	12	281	-299
2	13	192	173
2	16	282	302
2	19	132	113
3	-20	147	-120

K	L	FOBS	FCAL
3	-19	216	-245
3	-18	137	-167
3	-17	436	437
3	-16	214	178
3	-15	551	563
3	-11	223	-210
3	-10	158	160
3	-9	1276	-1283
3	-8	1417	-1406
3	-6	392	-328
3	-5	1022	1025
3	-4	1057	1078
3	-3	837	888
3	-2	772	-763
3	-1	669	695
3	0	141	122
3	1	1256	-1196
3	2	604	604
3	3	1121	-1073
3	4	1107	-1072
3	5	543	550
3	6	239	-188
3	7	360	369
3	8	479	455
3	9	471	494
3	10	603	608
3	11	325	-298
3	12	141	-154
3	13	640	-642
3	14	423	-415
3	17	128	159
3	18	200	-186
3	19	200	192
4	-19	322	-286
4	-17	497	-476
4	-16	295	-301
4	-15	384	370
4	-13	485	484
4	-12	128	-118
4	-10	412	400
4	-8	178	186
4	-7	1258	-1247
4	-6	942	-908
4	-5	876	-850
4	-3	488	486

K	L	FOBS	FCAL
4	-2	216	177
4	-1	1184	1157
4	0	166	-166
4	1	287	260
4	2	1196	1155
4	3	1363	-1308
4	4	123	129
4	5	376	-361
4	6	735	-702
4	7	185	182
4	8	477	-458
4	9	291	-299
4	11	997	944
4	12	416	391
4	13	155	108
4	15	547	-552
5	-18	245	264
5	-17	471	-454
5	-15	288	-305
5	-14	346	-412
5	-13	333	325
5	-10	159	-147
5	-9	335	372
5	-8	342	361
5	-7	158	146
5	-6	716	721
5	-5	868	-864
5	-4	235	251
5	-3	240	-264
5	-2	673	-693
5	-1	203	-193
5	0	667	-661
5	1	1320	1298
5	2	422	427
5	4	792	776
5	5	982	-961
5	6	310	-297
5	7	186	200
5	8	266	238
5	9	473	-457
5	10	312	-317
5	12	392	-322
5	13	674	614
5	14	207	191
5	16	288	288

K	L	FOBS	FCAL
5	17	281	-273
6	-17	192	186
6	-16	355	359
6	-15	352	-382
6	-12	211	-205
6	-10	133	76
6	-8	380	-266
6	-7	725	778
6	-6	384	-368
6	-5	614	-628
6	-4	708	730
6	-3	383	-340
6	-2	583	585
6	0	539	-540
6	1	462	-461
6	2	808	-799
6	3	737	795
6	4	534	541
6	5	137	148
6	6	139	88
6	7	358	-346
6	8	133	123
6	9	144	-129
6	10	391	394
6	11	450	-466
6	12	143	-119
6	13	287	199
6	14	481	-394
6	16	136	121
7	-15	144	-143
7	-9	394	-394
7	-7	378	374
7	-6	158	-92
7	-5	750	767
7	-4	281	-265
7	-3	974	-1003
7	-2	191	188
7	-1	346	350
7	0	471	458
7	3	293	-294
7	4	246	-236
7	5	353	353
7	7	178	171
7	10	278	256
7	11	347	-381

K	L	FOBS	FCAL
7	12	223	182
8	-13	157	-175
8	-10	177	187
8	-9	187	-146
8	-7	458	-476
8	-5	611	614
8	-2	217	204
8	-1	428	-439
8	0	265	-366
8	1	228	191
8	3	252	-260
8	4	338	343
8	5	188	-130
8	7	326	331
8	8	352	-365
8	11	129	74
9	-7	191	-205
9	-6	170	-177
9	-3	268	281
9	-2	306	345
9	0	298	305
9	1	195	210
9	2	358	-374
9	4	244	-249
9	5	488	-491
9	6	261	255
9	7	263	263
10	0	202	211
10	2	335	369
10	3	436	412

H = 4

K	L	FOBS	FCAL
0	-18	371	-355
0	-16	627	599
0	-14	1016	1012
0	-12	974	-1012
0	-10	601	-620
0	-6	529	-537
0	-4	2011	2065
0	-2	819	846
0	0	850	828
0	2	1082	-1180
0	4	514	-518
0	6	1376	1478

K	L	FOBS	FCAL
0	8	149	172
0	10	118	127
0	12	237	296
0	14	710	-757
0	16	425	450
1	-18	391	-360
1	-16	551	-596
1	-14	732	730
1	-12	720	727
1	-11	283	280
1	-10	155	-169
1	-9	168	132
1	-8	178	-217
1	-7	587	-579
1	-6	1067	-1071
1	-5	372	394
1	-4	152	-159
1	-3	416	-425
1	-2	996	1064
1	-1	255	-212
1	0	656	751
1	1	596	623
1	2	444	442
1	3	170	-160
1	4	1176	-1200
1	5	1037	-1044
1	6	698	-683
1	8	641	631
1	9	313	331
1	10	108	107
1	12	573	567
1	13	153	146
1	14	205	197
1	16	506	-521
1	19	187	-164
2	-16	301	-269
2	-14	379	-388
2	-13	486	-477
2	-12	321	315
2	-10	422	433
2	-9	798	796
2	-8	1158	1146
2	-6	147	83
2	-5	555	-532
2	-4	1572	-1618

K	L	FOBS	FCAL
2	-3	245	269
2	-1	671	-695
2	0	582	691
2	1	167	146
2	3	1217	1176
2	4	1172	1160
2	6	765	-741
2	7	389	-387
2	8	548	-562
2	9	225	-229
2	10	146	95
2	11	160	63
2	14	416	430
2	15	183	217
2	17	168	158
3	-20	143	161
3	-17	365	350
3	-16	154	163
3	-15	140	-194
3	-11	183	-185
3	-10	455	-452
3	-9	175	-158
3	-7	1097	1108
3	-6	1513	1543
3	-5	235	227
3	-4	130	-108
3	-3	190	-165
3	-2	988	-1017
3	-1	268	-240
3	0	533	560
3	1	768	-795
3	2	533	-533
3	3	233	237
3	4	391	380
3	5	399	372
3	6	823	803
3	7	102	85
3	8	125	-146
3	9	139	153
3	10	368	-332
3	11	508	-500
3	12	204	-215
3	13	170	-123
3	15	153	169
3	18	142	-132

K	L	FOBS	FCAL
4	-19	239	-236
4	-17	418	395
4	-15	175	184
4	-13	463	-494
4	-10	260	287
4	-8	397	-377
4	-7	372	-372
4	-5	663	639
4	-4	698	724
4	-3	470	494
4	-2	265	-312
4	-1	132	148
4	0	345	373
4	1	681	-688
4	2	560	567
4	4	401	-397
4	5	329	292
4	7	171	-190
4	9	403	406
4	11	451	431
4	12	194	205
4	13	565	-545
4	14	140	-142
4	17	240	218
5	-17	327	-328
5	-16	167	-218
5	-15	467	470
5	-13	125	-178
5	-11	445	-445
5	-10	308	-248
5	-9	244	295
5	-8	432	465
5	-7	512	-543
5	-6	455	482
5	-5	253	-303
5	-4	289	-289
5	-3	320	334
5	-2	381	-392
5	0	459	-445
5	1	131	-82
5	2	482	502
5	3	1048	-1053
5	5	121	122
5	6	190	165
5	7	207	177

K	L	FOBS	FCAL
5	8	258	-224
5	9	345	-339
5	10	508	-486
5	11	501	484
5	12	190	177
5	14	334	336
5	15	416	-381
5	16	166	-110
6	-15	175	-171
6	-13	323	329
6	-12	291	303
6	-10	272	-293
6	-9	268	282
6	-8	584	-583
6	-7	432	-414
6	-6	424	402
6	-5	719	-764
6	-4	625	653
6	-3	509	516
6	-2	167	-177
6	0	636	-649
6	1	295	352
6	3	180	191
6	4	154	-159
6	5	625	-601
6	8	540	498
6	11	159	122
6	13	260	229
6	14	126	99
7	-15	234	-229
7	-14	145	119
7	-10	224	257
7	-9	300	324
7	-8	239	-252
7	-7	616	613
7	-6	183	-263
7	-5	930	-948
7	-3	326	-296
7	-2	333	315
7	-1	676	685
7	0	206	203
7	1	356	-338
7	3	348	361
7	5	240	278
7	6	191	-164

K	L	FOBS	FCAL
7	7	465	-462
7	9	285	-282
7	10	386	240
7	13	224	236
8	-12	228	223
8	-11	167	-173
8	-9	138	-115
8	-7	538	548
8	-6	175	193
8	-5	460	490
8	-3	655	-745
8	-2	265	-279
8	2	391	401
8	3	172	-112
8	5	566	567
8	6	223	-224
8	7	137	147
8	9	324	-310
9	-7	185	-218
9	-5	389	412
9	-4	217	251
9	-3	285	317
9	-1	169	-155
9	0	326	-386
9	1	211	-230
9	2	187	-172
9	3	428	-469
9	4	228	289
9	5	211	154
9	7	371	393

H = 5

K	L	FOBS	FCAL
0	-18	480	446
0	-16	846	814
0	-14	561	-477
0	-12	929	-9[illegible]
0	-10	785	717
0	-8	191	-213
0	-6	1200	1226
0	-4	1054	1154
0	-2	942	-974
0	0	1193	-1255
0	2	494	-477
0	4	1049	1099

K	L	FOBS	FCAL
0	6	503	540
0	8	566	-603
0	10	124	-63
0	12	869	-897
0	14	320	-312
0	16	548	593
0	18	149	136
1	-17	322	-364
1	-16	382	394
1	-14	892	860
1	-13	226	263
1	-12	592	-600
1	-10	290	-306
1	-9	134	-82
1	-8	286	-292
1	-7	184	136
1	-6	401	-402
1	-5	297	-272
1	-4	1536	1504
1	-3	920	-930
1	-2	601	657
1	-1	446	484
1	1	164	152
1	2	885	-913
1	3	590	-595
1	4	1068	-1094
1	6	698	741
1	7	536	556
1	8	614	653
1	9	241	-280
1	10	176	228
1	12	217	193
1	13	136	149
1	14	648	-665
1	17	138	-133
2	-19	311	320
2	-16	191	-166
2	-15	196	-175
2	-14	169	88
2	-13	193	-220
2	-12	461	476
2	-11	132	145
2	-8	217	-207
2	-6	1223	-1212
2	-5	561	580

K	L	FOBS	FCAL
2	-4	144	-167
2	-3	294	-318
2	-2	763	823
2	-1	787	-872
2	1	798	823
2	2	535	546
2	4	197	-195
2	5	226	-228
2	6	1450	-1440
2	7	183	192
2	8	481	492
2	10	399	411
2	11	227	-234
2	12	405	393
2	15	120	162
2	16	292	-289
3	-16	136	-92
3	-13	325	325
3	-11	446	-453
3	-9	212	-190
3	-8	469	499
3	-6	131	-121
3	-4	1219	-1266
3	-3	136	119
3	-2	476	491
3	1	118	-142
3	2	198	-175
3	3	200	184
3	4	958	986
3	5	146	-124
3	6	330	-320
3	7	412	395
3	8	696	-683
3	9	228	243
3	10	147	115
3	11	284	-275
4	-15	485	-489
4	-13	359	386
4	-11	670	685
4	-10	462	430
4	-9	494	-521
4	-8	225	-241
4	-7	204	147
4	-6	418	399
4	-5	305	313

K	L	FOBS	FCAL
4	-4	268	-280
4	-1	225	235
4	0	441	458
4	1	314	352
4	2	130	-160
4	3	299	279
4	4	133	-134
4	5	294	-289
4	6	303	-271
4	7	158	-151
4	8	437	-442
4	9	504	492
4	10	126	68
4	15	265	256
5	-17	143	178
5	-13	482	-457
5	-12	276	-240
5	-11	411	443
5	-10	205	208
5	-9	257	212
5	-8	598	578
5	-7	164	-141
5	-6	203	-231
5	-5	394	394
5	-4	190	-147
5	-3	319	-308
5	-2	169	-170
5	-1	467	-497
5	2	319	333
5	3	172	176
5	4	177	172
5	5	408	383
5	7	259	-217
5	8	518	-479
5	10	173	-101
5	11	122	87
5	12	319	312
5	13	369	-335
5	15	182	177
6	-15	329	360
6	-14	151	208
6	-11	246	-228
6	-10	499	-492
6	-8	369	356
6	-7	407	-446

K	L	FOBS	FCAL
6	-6	253	266
6	-5	560	561
6	-3	413	427
6	-1	334	-332
6	0	182	-216
6	2	379	-368
6	3	518	-516
6	5	153	-109
6	6	717	701
6	7	443	433
6	8	142	134
6	9	129	106
6	10	525	-492
7	-13	323	302
7	-12	168	134
7	-11	200	192
7	-10	165	-228
7	-8	375	-404
7	-7	419	-442
7	-5	520	-527
7	-3	634	633
7	-2	193	190
7	1	227	218
7	2	167	-208
7	3	382	393
7	4	400	-403
7	5	615	-622
7	7	248	-262
7	8	312	304
7	9	457	458
7	10	141	125
8	-9	359	370
8	-7	393	423
8	-6	173	-187
8	-5	451	-450
8	-4	245	-255
8	-3	341	-412
8	-2	156	141
8	-1	281	277
8	0	282	295
8	3	389	415
8	4	159	-184
8	5	222	249
8	7	501	-524
9	-6	230	183

K	L	FOBS	FCAL
9	-5	427	469
9	-4	147	-151
9	-3	241	-267
9	-2	245	-272
9	-1	304	-338
9	0	143	116
9	1	158	-126
9	2	174	283

H = 6

K	L	FOBS	FCAL
0	-18	388	338
0	-16	282	-292
0	-14	824	-799
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0	-6	985	954
0	-4	1052	-1086
0	-2	498	-545
0	0	376	401
0	2	513	541
0	4	447	469
0	6	484	-539
0	8	175	-201
0	10	291	-291
0	14	516	538
0	16	187	147
1	-19	226	-217
1	-16	442	388
1	-15	146	185
1	-14	155	-112
1	-12	575	-548
1	-11	135	92
1	-10	394	394
1	-9	218	206
1	-8	452	-476
1	-7	159	-129
1	-6	724	734
1	-5	773	-764
1	-4	655	665
1	-3	264	264
1	-2	768	-859
1	-1	609	660
1	0	412	-446
1	1	103	86
1	2	174	-162

K	L	FOBS	FCAL
1	3	123	101
1	4	223	-210
1	6	685	642
1	7	423	-450
1	8	320	-350
1	11	390	400
1	12	350	-336
1	16	348	266
2	-17	202	-184
2	-14	297	301
2	-13	227	-193
2	-10	269	-284
2	-9	505	508
2	-8	279	-315
2	-7	465	504
2	-6	148	-137
2	-5	463	-452
2	-4	571	612
2	-3	995	-1052
2	-2	211	-225
2	-1	161	170
2	0	444	-497
2	1	505	543
2	3	215	-191
2	4	1084	-1028
2	5	404	418
2	6	365	320
2	7	222	-239
2	8	438	-418
2	9	650	-640
2	13	273	275
2	14	199	-196
2	16	142	-111
3	-18	136	117
3	-17	141	118
3	-15	348	373
3	-13	315	-291
3	-12	338	323
3	-11	559	-526
3	-10	298	-274
3	-9	120	117
3	-8	354	-306
3	-7	375	373
3	-6	547	-504
3	-5	584	508
3	-4	536	563
3	-2	363	396
3	-1	586	-672
3	0	581	-627
3	1	123	-131
3	2	425	438
3	3	209	-206
3	4	159	144
3	5	392	403
3	6	812	-799
3	7	446	448
3	8	424	418
3	9	306	-318
3	10	162	141
3	11	323	-332
3	14	116	-83
4	-15	213	196
4	-14	137	-158
4	-13	567	550
4	-12	278	241
4	-11	469	-464
4	-10	137	96
4	-9	451	-467
4	-8	204	-218
4	-7	257	245
4	-6	216	-221
4	-5	296	-307
4	-4	446	-457
4	-3	461	466
4	-2	541	564
4	-1	788	701
4	0	310	299
4	1	548	-572
4	2	226	-280
4	3	619	-608
4	4	195	-183
4	6	447	-423
4	7	459	445
4	8	191	-169
4	9	321	320
4	10	303	292
4	11	176	-173
4	13	145	124
5	-15	436	-416
5	-14	351	-313
5	-13	265	252
5	-11	449	415
5	-10	387	370
5	-9	250	-230
5	-5	207	-199
5	-3	580	-582
5	-2	654	-623
5	-1	625	621
5	1	507	527
5	2	499	454
5	4	264	247
5	5	302	-298
5	6	318	-302
5	7	294	-314
5	8	479	-451
5	9	211	179
5	10	235	173
5	12	122	181
6	-13	458	-460
6	-12	489	-488
6	-9	188	179
6	-8	338	357
6	-7	269	280
6	-6	152	-82
6	-5	302	345
6	-4	249	227
6	-3	572	-546
6	-1	304	-313
6	0	509	-513
6	2	136	-137
6	4	498	498
6	5	496	495
6	6	274	288
6	8	343	-343
6	9	389	-372
6	10	193	-148
7	-11	180	-160
7	-10	313	-343
7	-9	243	-224
7	-7	153	-163
7	-6	138	130
7	-5	439	430
7	-4	264	298
7	-3	389	399
7	-2	156	93
7	-1	260	-231
7	1	232	222
7	2	251	-238
7	3	346	-355
7	5	286	-266
7	6	230	209
7	7	550	532
7	8	177	178
8	-7	211	-192
8	-6	232	-252
8	-5	278	-319
8	-4	149	167
8	-3	235	221
8	-2	158	229
8	-1	171	162
8	1	235	215
8	3	295	309
8	5	408	-382
H = 7			
0	-16	137	-146
0	-14	252	235
0	-10	620	-601
0	-8	871	912
0	-4	641	-710
0	-2	630	659
0	0	161	-148
0	2	106	-127
0	4	107	126
0	6	122	94
0	10	149	-151
0	12	178	172
1	-15	148	-135
1	-14	193	-202
1	-13	237	251
1	-12	321	293
1	-11	431	435
1	-9	461	-420
1	-8	319	-337
1	-7	437	-459
1	-6	637	632
1	-5	343	332
1	-4	218	-251
1	-3	664	700
1	-1	139	-176
1	0	428	427
1	2	312	-328
1	4	195	197
1	5	432	-455
1	6	186	68
1	[illegible]	519	523
1	12	136	-70
1	13	169	-192
1	14	154	176
2	-17	142	-96
2	-15	199	-168
2	-13	137	-129
2	-12	388	-381
2	-11	404	400
2	-10	236	275
2	-9	416	404
2	-8	238	227
2	-7	454	-456
2	-5	663	-680
2	-4	161	-195
2	-2	397	-411
2	-1	509	539
2	0	489	539
2	2	269	-249
2	3	251	239
2	4	139	-127
2	5	135	-123
2	6	544	522
2	7	687	-664
2	8	159	-188
2	11	414	401
2	12	180	200
2	14	124	-110
3	-16	153	-143
3	-15	140	-91
3	-14	158	181
3	-13	465	[illegible]
3	-12	144	-163
3	-10	444	-437
3	-9	375	372
3	-7	363	340
3	-6	327	319
3	-5	340	356
3	-4	311	318
3	-3	536	-529
3	-2	496	-531
3	-1	501	-525
3	0	162	-162
3	1	434	453
3	2	231	233
3	3	385	354
3	4	468	-470
3	5	259	245
3	6	360	317
3	7	225	-225
3	8	269	250
3	9	436	-431
3	10	404	-386
4	-15	417	381
4	-14	146	96
4	-13	194	-178
4	-12	194	218
4	-11	548	-537
4	-10	293	-298
4	-8	161	-129
4	-6	210	-172
4	-5	221	195
4	-4	265	270
4	-3	627	638
4	-2	548	556
4	-1	615	-605
4	0	219	-208
4	1	682	-660
4	2	169	[illegible]
4	3	288	248
4	4	295	-270
4	5	216	191
4	6	216	-197
4	7	309	300
4	8	401	384
4	9	150	-86
4	10	182	134
4	12	146	-135
5	-13	555	498
5	-12	438	393
5	-11	247	-242
5	-9	383	-374
5	-8	218	-207
5	-6	294	-308

K	L	FOBS	FCAL
5	-4	384	-388
5	-3	355	338
5	-1	562	543
5	0	640	622
5	1	452	-435
5	2	174	166
5	3	258	-269
5	4	122	-136
5	5	285	-295
5	6	358	-357
5	9	265	271
6	-11	392	354
6	-10	407	388
6	-5	318	-316
6	-3	396	-418
6	-2	444	-458
6	-1	368	348
6	0	253	-224
6	2	310	283
6	4	252	254
6	7	416	-406
6	8	155	-104
7	-9	192	184
7	-8	122	100
7	-4	158	164
7	-3	305	-299
7	0	151	-176
7	1	144	157
7	2	123	-98
7	3	278	-264
7	4	130	84
7	5	287	270
7	6	153	133
8	-1	158	-155

H = 8

K	L	FOBS	FCAL
0	-12	459	-469
0	-10	253	228
0	-8	708	702
0	-6	431	-370
0	-4	327	337
0	-2	247	-258

K	L	FCBS	FCAL
0	0	607	-591
0	2	526	517
0	4	522	544
0	6	130	-132
0	8	223	-182
0	10	179	-145
1	-16	199	167
1	-14	222	225
1	-13	276	280
1	-11	296	-302
1	-10	597	-591
1	-9	272	-262
1	-8	172	159
1	-7	162	195
1	-6	285	266
1	-5	224	241
1	-2	463	488
1	0	485	-513
1	2	420	-431
1	3	364	-378
1	4	181	188
1	6	175	156
1	7	386	345
1	8	157	139
1	11	215	-187
1	12	185	-186
2	-15	136	-113
2	-13	271	265
2	-12	235	224
2	-11	283	290
2	-10	292	282
2	-9	282	-249
2	-8	416	-394
2	-7	424	-422
2	-6	169	-111
2	-5	175	-94
2	-3	214	245
2	-2	206	204
2	-1	256	272
2	0	328	335
2	1	143	111
2	2	116	-130
2	4	119	140

K	L	FOBS	FCAL
2	5	548	-547
2	6	169	-140
2	8	164	-149
2	9	387	367
2	10	459	440
3	-15	208	-218
3	-13	147	-142
3	-12	231	-233
3	-11	397	388
3	-10	248	237
3	-9	228	218
3	-8	332	346
3	-5	317	-312
3	-4	159	-111
3	-3	582	-600
3	-2	236	-231
3	-1	216	233
3	0	195	177
3	1	399	402
3	4	305	283
3	6	300	314
3	7	449	-408
3	8	440	-423
3	10	173	-154
4	-13	384	-365
4	-12	162	-102
4	-10	268	-247
4	-9	253	244
4	-8	188	194
4	-5	503	517
4	-4	235	243
4	-3	213	-199
4	-1	650	-652
4	0	134	-138
4	1	374	370
4	3	285	277
4	5	198	175
4	6	272	255
4	7	176	129
4	8	505	259
4	9	211	-189
4	10	228	-234
5	-12	177	167

K	L	FOBS	FCAL
5	-11	317	-309
5	-10	156	-113
5	-9	203	158
5	-4	189	-159
5	-3	539	548
5	-2	418	406
5	-1	418	-417
5	1	444	-454
5	2	176	-177
5	3	151	127
5	7	253	217
6	-9	293	-314
6	-6	213	217
6	-4	335	-326
6	-3	227	228
6	-2	162	-162
6	-1	153	170
6	0	268	268
6	1	324	-272
6	5	179	-183
7	-1	246	-249
7	0	184	-133
7	1	146	-159

H = 9

K	L	FOBS	FCAL
0	-14	209	-213
0	-10	667	590
0	-6	185	-196
0	-4	249	-280
0	-2	565	-610
0	0	631	631
0	2	897	868
0	4	294	-309
0	6	365	-376
0	8	255	-229
1	-12	408	-373
1	-11	179	-162
1	-9	164	150
1	-8	638	638
1	-6	133	153
1	-4	243	208
1	-2	330	-328

K	L	FCBS	FCAL
1	0	665	-674
1	1	287	-285
1	3	329	336
1	4	525	529
1	5	252	247
2	-13	222	235
2	-11	208	-201
2	-10	488	-468
2	-8	320	-317
2	-7	160	164
2	-6	349	343
2	-4	159	96
2	-2	237	230
2	0	200	-161
2	2	366	-336
2	3	288	-270
2	7	278	239
2	8	353	358
3	-12	157	149
3	-10	283	291
3	-8	383	-393
3	-6	284	-274
3	-5	176	-182
3	-2	169	98
3	-1	244	228
3	5	185	-145
3	6	196	-187
3	7	170	-152
3	8	218	-217
4	-8	169	-100
4	-7	200	164
4	-3	425	-436
4	-1	259	269
4	0	142	135
4	1	334	317
4	3	217	-225
4	6	155	125
5	-7	172	-162
5	-6	208	-272
5	-5	218	201
5	-2	178	153
5	-1	290	-305
5	0	164	-146

K	L	FOBS	FCAL
5	1	410	410
5	2	129	91

H = 10

K	L	FOBS	FCAL
0	-10	139	-106
0	-8	385	-340
0	-4	165	-175
0	0	625	581
0	2	225	-236
0	4	402	-401
1	-7	174	-147
1	-6	237	-234
1	-5	125	129
1	-4	151	-94
1	-3	149	142
1	-2	344	-358
1	-1	[illegible]	-145
1	0	161	172
1	1	124	-113
1	2	523	499
1	3	109	106
1	4	111	-100
2	-9	149	122
2	-8	386	403
2	-7	249	-246
2	-6	291	286
2	-5	144	-167
2	-4	127	-127
2	-3	273	246
2	-1	156	124
2	0	301	-296
2	2	127	126
2	3	152	-148
3	-6	307	327
3	-5	288	-277
3	-2	146	-104
3	1	130	98
3	2	148	-77
3	3	123	149

TABLE D-2

FINAL POSITIONAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS[a]

FOR XYLENEENNEACARBONYLTETRACOBALT[b]

ATOM NAME	X	Y	Z
Co1	0.79997(12)	0.28372(14)	0.31044(6)
Co2	0.89898(12)	0.16564(14)	0.41097(7)
Co3	0.69311(13)	0.07858(13)	0.34877(7)
Co4	0.68542(12)	0.29049(14)	0.41342(7)
C1	0.4764(10)	0.3323(12)	0.4292(7)
C2	0.5408(13)	0.4497(12)	0.4054(7)
C3	0.6633(15)	0.4966(13)	0.4434(8)
C4	0.7220(13)	0.4246(16)	0.4970(7)
C5	0.6569(14)	0.3079(16)	0.5182(7)
C6	0.5392(12)	0.2594(13)	0.4834(6)
C7	0.3448(16)	0.2824(18)	0.3912(8)
C8	0.4804(34)	0.5266(37)	0.3536(17)
C9	0.7155(40)	0.6234(44)	0.4172(20)
C11	0.8843(12)	0.2265(12)	0.2433(6)
O11	0.9392(12)	0.1840(11)	0.2006(5)
C12	0.7606(11)	0.4513(12)	0.2799(5)
O12	0.7380(10)	0.5573(9)	0.2600(5)
CB1	0.9404(12)	0.3395(11)	0.3727(5)
OB1	1.0153(9)	0.4306(9)	0.3890(5)
C21	1.0264(11)	0.0614(12)	0.3838(6)
O21	1.1109(8)	-0.0020(10)	0.3652(5)
C22	0.9734(11)	0.2073(11)	0.4935(6)
O22	1.0177(10)	0.2376(11)	0.5448(5)
CB2	0.7745(9)	0.0363(12)	0.4384(6)
OB2	0.7511(9)	-0.0318(9)	0.4835(4)

TABLE D-2 (CONT'D)

C31	0.7585(13)	-0.0492(13)	0.2990(6)
O31	0.8070(11)	-0.1251(9)	0.2658(5)
C32	0.5391(14)	0.0022(11)	0.3612(6)
O32	0.4416(9)	-0.0510(10)	0.3726(5)
CB3	0.6202(12)	0.2146(12)	0.2867(6)
OB3	0.5229(9)	0.2451(10)	0.2534(5)
H4	0.8081	0.4538	0.5203
H5	0.6955	0.2602	0.5583
H6	0.5002	0.1740	0.4968

[a] Estimated standard deviations are right justified to the least significant digits of the fractional co-ordinates.

[b] See Figure V-C-1 , page 300 in the text for a description of the numbering scheme used.

TABLE D-3

FINAL THERMAL PARAMETERS[a] ($x10^4$) WITH ESTIMATED STANDARD DEVIATIONS[b]

FOR XYLENEENNEACARBONYLTETRACOBALT[c]

ATOM NAME	B or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co1	94.9(14)	66.8(15)	24.8(4)	5.3(14)	10.5(6)	4.0(7)
Co2	84.0(14)	75.9(16)	25.2(4)	15.1(13)	5.0(6)	0.6(7)
Co3	96.2(15)	63.9(15)	24.2(4)	-1.9(13)	7.9(6)	0.0(7)
Co4	89.4(14)	77.1(16)	26.0(4)	14.3(14)	11.4(6)	-6.6(7)
C1	89(12)	122(15)	45(5)	-1(12)	25(6)	-32(7)
C2	132(17)	114(14)	37(5)	49(13)	14(7)	-6(7)
C3	171(20)	93(16)	62(6)	-6(15)	42(9)	-37(8)
C4	142(17)	178(21)	41(17)	44(17)	20(7)	-29(8)
C5	150(18)	179(23)	39(5)	8(18)	46(8)	-17(9)
C6	135(16)	156(18)	28(4)	48(14)	10(6)	-12(7)
C7	102(23)	242(26)	65(6)	1(23)	-4(10)	-27(11)
C11	170(17)	97(14)	39(4)	-3(13)	36(7)	20(7)
O11	360(20)	186(16)	60(4)	-21(15)	95(8)	-22(7)
C12	138(14)	99(14)	29(3)	10(12)	6(6)	16(6)
O12	226(14)	135(11)	60(4)	33(11)	29(6)	37(6)

TABLE D-3 (CONT'D)

CB1	165(16)	82(12)	34(4)	9(13)	8(6)	19(6)
OB1	186(13)	137(12)	67(4)	-67(12)	-23(6)	18(6)
C21	79(12)	121(16)	35(4)	-16(12)	8(6)	8(7)
O21	127(11)	191(15)	52(4)	32(11)	18(5)	0(6)
C22	141(15)	102(13)	40(4)	10(12)	-11(7)	0(7)
O22	247(15)	218(17)	44(3)	59(14)	-38(6)	-30(6)
CB2	69(10)	105(15)	39(4)	13(10)	6(5)	6(7)
OB2	182(12)	155(13)	35(3)	-9(11)	17(5)	29(5)
C31	169(18)	118(16)	25(4)	7(14)	12(6)	-8(6)
O31	274(16)	157(12)	57(4)	31(12)	25(6)	-47(6)
C32	157(18)	81(12)	31(4)	5(13)	11(6)	5(5)
O32	152(11)	185(14)	55(4)	-58(11)	29(5)	9(6)
CB3	142(16)	83(13)	35(4)	-10(14)	15(4)	8(6)
OB3	164(11)	207(15)	54(4)	-40(11)	-37(16)	51(6)
C8	968⁰⁰(129⁰⁰)					
C9	119⁰⁰(148⁰⁰)					

a These are applied in the expression $\exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$.

b Estimated standard deviations are right justified to the least significant digits of the thermal parameter ($\times 10^4$).

c See Figure V-C-1 , page 300 in the text for a description of the numbering used.

APPENDIX E

TABLE E-1: The observed and calculated structure factors for benzeneenneacarbonyltetracobalt.

TABLE E-2: Final positional parameters with estimated standard deviations for benzeneenneacarbonyltetracobalt.

TABLE E-3: Final thermal parameters (x10^4) with estimated standard deviations for benzeneenneacarbonyltetracobalt.

TABLE E-1

THE OBSERVED AND CALCULATED STRUCTURE FACTORS FOR BENZENEENNEACARBONYLTETRACOBALT

K	L	FOBS	FCAL
	H =	0	
8	0	251	284
9	0	388	282
10	0	240	387
	H =	1	
0	-10	234	125
0	-9	265	267
0	-8	211	167
0	-1	1651	1549
0	0	158	184
1	-10	386	257
1	-9	241	227
1	-1	288	283
1	0	1521	1543
1	1	473	494
8	-1	143	164
8	0	172	176
8	1	291	276
9	-1	268	137
9	0	259	282
9	1	184	193
10	-1	132	97
10	0	167	115
10	1	244	225
	H =	2	
-1	-10	192	127
-1	-9	115	117
-1	-8	151	143
-1	-1	652	640
-1	1	158	139
0	-2	588	557
0	-1	714	675
0	0	582	537
0	1	234	216
1	-9	129	120
1	-2	927	889
1	-1	537	511
1	0	43	41
1	1	324	313
2	-8	280	283
2	-2	688	669
2	-1	459	461
2	0	238	257
2	1	1073	1117
2	2	925	955
8	0	205	161
9	-2	189	187
9	0	117	115
9	1	134	148
10	-1	321	308
	H =	3	
-2	-9	261	245
-2	-2	289	213
-2	-1	341	335
-2	0	558	558
-2	1	766	747
-2	2	297	295
-1	-8	273	266
-1	-3	528	513
-1	-2	126	126
-1	-1	129	117
-1	0	523	519
-1	1	791	757
-1	2	310	287
0	-9	169	144
0	-8	181	168
0	-3	386	382
0	-2	1142	1108
0	-1	955	924
0	0	457	462
0	1	125	145
1	-9	119	126
1	-8	183	188
1	-3	1192	1188
1	-2	371	369
1	-1	305	297
1	0	202	208
1	1	374	343
1	2	184	189
2	-9	116	99
2	-2	1043	1048
2	-1	235	245
2	0	271	262
2	1	497	585
2	2	983	939
3	-8	155	163
3	-3	380	391
3	-2	181	170
3	-1	717	738
3	0	79	77
3	1	241	257
3	2	724	762
3	3	413	414
8	1	212	280
8	3	388	389
9	-3	199	189
9	-1	389	389
9	0	138	120
9	2	174	165
10	0	227	219
10	3	146	126
	H =	4	
-3	-4	258	265
-3	-3	530	542
-3	-2	284	282
-3	0	385	374
-3	1	356	358
-3	2	123	122
-3	3	99	93
-2	-8	319	321
-2	-4	274	270
-2	-3	212	214
-2	-2	476	482
-2	-1	567	561
-2	0	719	714
-2	1	227	210
-2	2	581	576
-2	3	552	547
-1	-9	169	214
-1	-8	283	293
-1	-4	90	89
-1	-3	144	137
-1	-1	98	99
-1	0	207	207
-1	1	1002	949
-1	2	578	572
-1	3	214	209
0	-9	227	267
0	-8	210	223
0	-3	744	737
0	-2	94	88
0	-1	687	692
0	0	299	291
0	1	543	542
0	2	1179	1160
0	3	437	438
1	-8	228	272
1	-4	712	786
1	-3	428	411
1	-2	1299	1280
1	-1	268	284
1	0	698	707
1	1	206	212
1	2	288	260
1	3	439	444
2	-4	197	185
2	-3	478	468
2	-2	558	569
2	-1	972	963
2	2	605	617
2	3	349	366
3	-8	178	168
3	-4	173	178
3	-3	225	227
3	-2	712	713
3	-1	169	183
3	0	183	171
3	1	498	497
3	2	357	366
3	3	994	1008
4	-8	124	128
4	-4	209	215
4	1	119	117
4	2	788	792
4	3	592	608
4	4	723	745
8	-3	147	128
9	-2	131	143
8	0	265	263
8	2	491	489
8	3	155	158
6	4	291	288
9	-2	358	344
9	0	288	198
9	1	324	323
9	3	392	348
9	4	138	185
10	2	212	212
	H =	5	
-4	-5	274	281
-4	-4	292	305
-4	-3	363	375
-4	-2	175	167
-4	-1	100	97
-4	0	161	170
-4	1	117	117
-4	3	262	264
-4	4	487	486
-3	-4	748	758
-3	-2	375	394
-3	-1	127	114
-3	2	523	538
-3	4	129	116
-2	-8	259	264
-2	-5	331	329
-2	-4	152	156
-2	-3	922	945
-2	-2	273	277
-2	-1	181	195
-2	1	774	771
-2	2	589	588
-2	3	567	571
-1	-8	152	129
-1	-5	246	299
-1	-4	388	382
-1	-3	118	125
-1	-2	455	464
-1	-1	218	232
-1	0	611	613
-1	1	763	759
-1	2	968	963
-1	3	463	467
-1	4	267	265
0	-8	369	371
0	-5	182	87
0	-4	335	336
0	-3	186	179
0	-2	458	449
0	-1	119	145
0	0	593	684
0	1	742	747
0	2	823	821
0	3	531	532
1	-5	136	139
1	-3	918	919
1	-2	492	497
1	-1	733	742
1	1	316	329
1	2	593	563
1	3	282	267
2	-4	457	462
2	-3	406	418
2	-2	683	675
2	-1	425	426
2	0	247	245
2	3	389	404
2	4	183	111
3	-5	128	147
3	-3	314	332
3	-2	368	382
3	-1	289	293
3	0	401	406
3	1	418	427
3	2	482	487
3	3	311	316
3	4	318	330
4	-3	89	92
4	0	339	338
4	1	148	132
4	2	329	338
4	3	539	543
5	-5	225	232
5	-4	225	224
5	-3	331	319
5	-2	262	260
5	-1	212	263
5	0	207	215
5	1	335	344
5	5	559	542

K	L	FOBS	FCAL
8	-3	269	271
8	-2	126	116
8	1	347	352
8	3	424	427
8	5	164	141
9	0	187	152
9	2	422	404
9	4	250	231

H = 6

K	L	FOBS	FCAL
-5	-5	102	116
-5	-3	116	149
-5	-2	151	148
-5	0	581	573
-5	1	171	166
-5	2	308	299
-5	3	131	136
-5	4	176	178
-4	-4	393	415
-4	-3	164	165
-4	-2	233	225
-4	-1	443	447
-4	1	406	402
-4	2	119	104
-4	4	129	119
-4	5	294	294
-3	-5	332	332
-3	-3	672	674
-3	-1	158	162
-3	0	264	271
-3	2	131	141
-3	3	262	265
-3	4	327	328
-3	5	333	315
-2	-6	142	135
-2	-5	171	171
-2	-4	611	597
-2	-2	626	657
-2	-1	132	131
-2	0	427	431
-2	1	236	250
-2	2	469	469
-2	3	215	207
-2	4	431	423
-2	5	415	406
-1	-6	240	232
-1	-5	258	259
-1	-3	504	507
-1	-2	189	203
-1	0	371	373
-1	1	763	764
-1	2	679	686
-1	3	505	519
-1	4	125	126
-1	5	223	222
0	-5	205	195
0	-4	94	79
0	-3	181	169
0	-2	173	178
0	-1	256	257
0	0	242	235
0	1	430	431
0	2	597	614
0	3	687	691
1	-6	227	225
1	-5	348	353
1	-4	208	201
1	-2	243	230
1	1	280	282
1	2	351	355
1	3	145	146
1	4	261	271
1	5	326	320
2	-6	201	197
2	-4	364	367
2	-2	303	296
2	-1	144	147
2	1	221	214
2	2	213	197
2	3	162	163
2	4	166	160
3	-5	296	285
3	-4	171	164
3	-2	160	164
3	-1	527	537
3	0	322	334
3	1	300	295
3	2	297	306
3	3	117	102
3	5	260	252
4	-4	387	313
4	-2	106	95
4	-1	373	377
4	0	388	389
4	1	622	637
4	2	157	165
4	3	248	256
4	5	237	232
5	-6	160	159
5	-5	104	171
5	-4	188	193
5	-3	400	395
5	-2	255	243
5	0	568	568
5	1	126	129
5	2	514	509
5	3	121	114
5	4	293	286
6	-5	120	114
6	-4	369	371
6	-3	272	275
6	-2	422	413
6	-1	238	248
6	0	129	104
6	1	361	357
6	2	135	130
6	5	339	331
6	6	118	82
8	-2	237	235
8	2	488	382
8	4	247	237
8	6	135	114
9	1	221	221
9	3	279	260

H = 7

K	L	FOBS	FCAL
-6	-2	117	91
-6	0	332	324
-6	2	193	185
-5	-4	147	129
-5	-2	117	108
-5	-1	350	335
-5	1	419	421
-5	2	203	201
-5	4	145	132
-5	5	176	187
-4	-5	231	236
-4	-3	204	204
-4	-2	201	205
-4	-1	178	192
-4	0	545	552
-4	1	124	132
-4	2	192	179
-4	4	132	135
-4	5	346	344
-4	6	189	197
-3	-5	127	134
-3	-4	418	434
-3	-2	294	297
-3	-1	342	336
-3	0	163	171
-3	1	345	326
-3	2	104	67
-3	4	241	247
-3	5	228	235
-3	6	482	396
-2	-5	216	199
-2	-3	617	631
-2	-2	124	130
-2	-1	186	191
-2	0	111	85
-2	2	253	241
-2	3	164	153
-2	5	357	360
-2	6	148	159
-1	-4	281	278
-1	-3	351	358
-1	-2	303	297
-1	-1	319	327
-1	0	362	365
-1	1	225	222
-1	3	239	232
-1	4	263	260
-1	5	124	138
-1	6	280	271
0	-6	124	102
0	-4	135	127
0	-2	196	197
0	-1	113	103
0	0	168	147
0	1	529	531
0	2	413	410
0	4	302	300
1	-6	204	226
1	-4	348	343
1	-3	108	79
1	-2	129	118
1	-1	166	172
1	0	246	248
1	3	502	500
1	4	406	391
1	6	198	192
2	-5	432	447
2	-4	162	148
2	-3	225	212
2	-2	164	163
2	0	323	326
2	2	124	117
2	3	412	405
2	4	141	144
2	5	530	515
2	6	216	215
3	-6	188	179
3	-5	221	211
3	-4	366	366
3	-3	243	227
3	-1	218	217
3	0	227	225
3	1	553	568
3	2	161	184
3	3	191	203
3	4	428	432
3	5	188	167
3	6	249	247
4	-5	163	175
4	-4	154	156
4	-3	275	274
4	-1	171	166
4	0	593	599
4	1	152	138
4	2	601	613
4	5	196	195
4	6	146	131
5	-5	124	112
5	-4	237	223
5	-2	218	215
5	-1	275	284
5	1	633	626
5	3	138	143
5	5	249	236
5	6	148	151
6	-3	313	306
6	-1	168	165
6	0	252	249
6	2	333	334
6	4	192	187
6	6	337	298
7	-2	276	276
7	2	135	137
7	5	234	218
7	6	256	229
8	3	195	137

TABLE E-2

FINAL POSITIONAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS[a] FOR BENZENEENNEACARBONYLTETRACOBALT[b]

ATOM NAME	X	Y	Z
Co1	0.30627(11)	0.18002(10)	0.39772(11)
Co4	0.18692(10)	0.18692(10)	0.18692(10)
C1	0.0364(13)	0.2263(10)	0.0444(14)
C2	-0.0213(10)	0.1596(14)	0.1682(14)
C11	0.3949(10)	0.2320(8)	0.5264(9)
O11	0.4494(8)	0.2707(7)	0.6107(7)
C12	0.2750(9)	0.0094(10)	0.4754(10)
O12	0.2536(7)	-0.0958(6)	0.5260(7)
CB1	0.4545(10)	0.1185(9)	0.2615(8)
OB1	0.5342(7)	0.0260(7)	0.2379(6)
H1	-0.0011	0.2975	0.0126
H2	-0.0887	0.1944	0.2136

a Estimated standard deviations are right justified to the least significant digits of the fractional co-ordinates.

b See Figure V-C-1 , page 300 in the text for a description of the numbering scheme used.

TABLE E-3

FINAL THERMAL PARAMETERS[a] ($x10^4$) WITH ESTIMATED STANDARD DEVIATIONS[b] FOR BENZENEENNEACARBONYLTETRACOBALT[c]

ATOM NAME	B or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co1	87.6(17)	75.1(17)	69.3(16)	-1.4(12)	-4.6(12)	3.0(12)
Co4	86.3(13)	86.3(13)	86.3(13)	-12.8(12)	-12.8(12)	-12.8(12)
C1	145(20)	148(17)	167(20)	-14(16)	-79(14)	-10(16)
C2	102(15)	171(21)	182(22)	-19(15)	-28(15)	-43(15)
C11	133(15)	80(14)	112(15)	13(10)	22(12)	19(11)
O11	246(14)	179(12)	159(12)	-36(10)	-84(10)	-27(9)
C12	85(12)	110(15)	140(16)	-4(11)	10(10)	-28(12)
O12	119(12)	86(10)	224(13)	-31(9)	9(10)	36(9)
CB1	136(15)	104(14)	94(13)	4(11)	26(11)	8(10)
OB1	197(12)	123(11)	148(10)	88(9)	50(8)	16(8)
H1	5.0					
H2	5.0					

a These are applied in the expression $\exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$.

b Estimated standard deviations are right justified to the least significant digits of the thermal parameter ($x10^4$).

c See Figure V-C-1 , page 300 in the text for a description of the numbering used.

APPENDIX F

TABLE F-1: Attempted reactions of transition metal carbonyls with $As(C{\equiv}CR)_3$, R = H, CH_3, t-Bu, Ph.

TABLE F-1

ATTEMPTED REACTIONS OF TRANSITION METAL CARBONYLS WITH $As(C\equiv CR)_3$, R = H, CH_3, t-Bu, Ph.

Reactant and # moles	Substrate and # moles	Solvent	Temp. °C	Time hours	Remarks
$1Cr(CO)_6$	$1As(C\equiv CH)_3$	CH_2Cl_2	Room	120	No product
$1Mo(CO)_6$	$2As(C\equiv CH)_3$	CH_2Cl_2	40	20	No product
$3Mo(CO)_6$	$1As(C\equiv CH)_3$	CH_2Cl_2	40	48	Brown intractible solid
$10Mo(CO)_6$	$1As(C\equiv CH)_3$	hexane	69	18	No product
$1Mo(CO)_6$	$1As(C\equiv CCH_3)_3$	hexane	69	72	Brown intractible solid
$1Mo(CO)_6$	$1As(C\equiv CCH_3)_3$	CH_2Cl_2	hν	1	No product
$1Mo(CO)_3(CH_3CN)_3$	$1As(C\equiv CCH_3)_3$	Ethanol	78	2	Brown intractible solid
$1\{CpMo(CO)_3\}_2$	$2As(C\equiv CCH_3)_3$	T.H.F.	hν	2	Yellow product- not identified.
$1W(CO)_3(CH_3CN)_3$	$1As(C\equiv CCH_3)_3$	hexane	69	2	Yellow intractible powder.
$1Mn_2(CO)_{10}$	$2As(C\equiv CH)_3$	hexane	69	3	No product
$1Mn_2(CO)_{10}$	$2As(C\equiv CCH_3)_3$	T.H.F.	hν	12	Colourless crystals, not characterized.

$37Fe(CO)_5$	$1As(C\equiv CCH_3)_3$	CH_2Cl_2	40	3	Positive pressure CO gas. No product
$3Fe_2(CO)_9$	$1As(C\equiv CH)_3$	CH_2Cl_2	40	5	Brown powder
$1Fe_2(CO)_9$	$2As(C\equiv CH)_3$	hexane	69	14	Brown powder - care was exercised to exclude oxygen. Product dried for four days. Chemical analysis report: %C = 39.94, 40.00 %H = 2.17, 2.22 %Fe = 8.60, 8.63 %As = 25.60, 25.47
$1Fe_2(CO)_9$	$1As(C\equiv CCH_3)_3$	hexane	69	1	Various fractions
$3Fe_2(CO)_9$	$1As(C\equiv CCH_3)_3$	CH_2Cl_2	40	0,2	Red plates - a) +Na Δ diglyme/KCl Nothing b) +Na Δ DMSO/$(CH_3)_4N^+I^-$ Nothing.
$1Fe_3(CO)_{12}$	$1As(C\equiv CH)_3$	cyclo-hexane	81	5	Brown powder
$1Fe_3(CO)_{12}$	$2As(C\equiv CH)_3$	hexane	69	16	Brown powder- care exercised to exclude oxygen. Dried for 7 days. Chemical analysis: %C = 31.64, 31.75 %H = 1.80, 1.67 %Fe = 19.01, 19.29 %As = 18.22, 18.38
$1Fe_3(CO)_{12}$	$2As(C\equiv CH)_3$	hexane	69	38	The same conditions as for the preceeding reaction but a different chemical analysis was obtained:

					%C = 26.84, 27.o2 %H = 1.96, 2.05 %Fe = 21.61, 21.67 %As = 14.42, 14.21
$3Fe_3(CO)_{12}$	$1As(C{\equiv}CH)_3$	CH_2Cl_2	40	72	Brown powder.
$10Fe_3(CO)_{12}$	$1As(C{\equiv}CH)_3$	hexane	69	24	Brown powder.
$1Fe_3(CO)_{12}$	$3As(C{\equiv}CCH_3)_3$	CH_2Cl_2	40	3-72	After 3 hours - yellow globules on sides of flask. Brown powder after 72 hours.
$1Fe_3(CO)_{12}$	$1As(C{\equiv}CCH_3)_3$	hexane	69	1-18	Gold band on chromatography after 1 hour. Brown powder not isolated.
$3Fe_3(CO)_{12}$	$1As(C{\equiv}CCH_3)_3$	hexane	Room	12	Nothing
$1Fe_3(CO)_{12}$	$1As(C{\equiv}Ct\text{-}bu)_3$	hexane	69	24	Brown powder
$3Fe_3(CO)_{12}$	$1As(C{\equiv}Ct\text{-}bu)_3$	hexane	69	24	Brown powder- qualitatively analyzed for As and Fe.
$3Fe_3(CO)_{12}$	$1As(C{\equiv}CPh)_3$	hexane	69	12	Chromatographed - product decomposed before identified
$CpFe(CO)_2I$	$1As(C{\equiv}CCH_3)_3$	hexane	69	5	Nothing
$2\{CpFe(CO)_2\}_2$	$1As(C{\equiv}CCH_3)_3$	CH_2Cl_2	h	1½	Some change did occur but product was not isolated.
$1Ru_3(CO)_{12}$	$1As(C{\equiv}CH)_3$	hexane	Room	5	No product observed
$1Ru_3(CO)_{12}$	$1As(C{\equiv}CH)_3$	CH_2Cl_2	40	5	Brown powder observed which believed to be oxidation product.

$1Ru_3(CO)_{12}$	$1As(C{\equiv}CCH_3)_3$	hexane	Room 69	72 4	Nothing observed to form at room temperature but brown decomposition product formed at higher temperature.
$1Co_2(CO)_8$	$2As(C{\equiv}CH)_3$	cyclo-hexane	Room	60	Red solution. Recovered solid identified as tris(hexa-carbonyldicobalt-π-ethynyl)-arsine. Brown powder also present.
$3Co_2(CO)_8$	$1As(C{\equiv}CH)_3$	cyclo-hexane	Room	2	Reported in this Thesis.
$3Co_2(CO)_8$	$1As(C{\equiv}CCH_3)_3$	CH_2Cl_2	Room	72	I.R. indicated the product was the analog of tris-(hexacarbonyldicobalt-π-ethynyl)arsine.
$3Co_2(CO)_8$	$1As(C{\equiv}CCH_3)_3$	hexane	69	15	Chemical alalysis: %As — 1.81 %Co — None or trace %C — 47.54 %H — 2.92
$3Co_2(CO)_8$	$1As(C{\equiv}CCH_3)_3$	hexane	Room	170	Chromatographed - 4 bands A- Red eluted with hexane B- Red-brown band - hexane C- Orange - hexane D- Brown band - CH_2Cl_2
$3Co_2(CO)_8$	$1As(C{\equiv}Ct\text{-}bu)_3$	benzene	80	12	Chromatographed - 2 bands A- Orange eluted with benzene B- Brown-red - benzene

$4Rh_4(CO)_{12}$	$1As(C\equiv CH)_3$	hexane	69	3	Black insoluble powder
$1\{Rh(CO)_2Cl\}_2$	$1As(C\equiv CCH_3)_3$	CH_2Cl_2	$h\nu$	1	Solution colour changed but no product was isolated.
$1\{CpNi(CO)\}_2$	$1As(C\equiv CCH_3)_3$	hexane	69	3	Nothing.

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